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**CHEMICAL SCAVENGER PROBE DETERMINATIONS OF
ATOM AND EXCITED MOLECULE CONCENTRATIONS
IN NONEQUILIBRIUM SUPERSONIC STREAMS
OF ACTIVE NITROGEN**

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A. Fontijn, D. E. Rosner and S. C. Kurzius

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CHEMICAL SCAVENGER PROBE DETERMINATIONS
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SUMMARY

A quartz chemical scavenger probe has been developed to study local active species concentrations in a gas expanded from a converging-diverging nozzle glow discharge source. The probe samples a small central portion of the supersonic non-equilibrium jet and thus allows direct comparison to other point measurement techniques for determining active species concentrations in the jet, e.g., catalytic detectors. The results obtained with active nitrogen at one relatively low discharge power output are discussed. The sampled gas mixed and reacted inside the probe with one of the scavenger gases NO, NH₃ or C₂H₄ at 18.8 mm Hg and an average temperature of 500°K. The NO light titration technique and the production of HCN from C₂H₄ set an upper and lower bound respectively for the atom concentration. The observed maximum amount of NO decomposition was 2.1 times as large as the NO light titration end point flow rate. This difference is far in excess of that observed in conventional discharge flow systems and is interpreted as being due to excited N₂ molecules reacting with NO in a reaction slow compared to that between N-atoms and NO. The contribution of these molecules to the energy content of the jet was found to be at least comparable to that of the N-atoms. A new analytical technique for quantitative analysis of the undecomposed NO was developed. Decomposition of NH₃ also showed the presence of excited molecules; however, since secondary H-atom attack appeared to occur, no calculation of the concentration of these molecules was possible from the NH₃ decomposition data alone.

It is shown to be likely that atom recombination before reaction inside the probe will not cause the measured relative concentration of atoms to be significantly lower than in the free jet. The nature of the excited molecules measured by the NO and NH₃ reactions is discussed. It is probable that the NH₃ reaction is predominantly due to N₂(A $^3\Sigma_u^+$) molecules. These molecules may also be responsible for the NO decomposition beyond the light titration end point. It is quite possible that de-excitation of N₂(A $^3\Sigma_u^+$) before reaction with the scavenger gas was insignificant, but if other excited molecules are involved the relative concentration of excited molecules determined by the probe may be lower than in the free jet. The influence of possible diffusional separation effects on the results is considered and found to be negligible.

It was shown that the NO light titration technique can also be used for composition measurements of the total supersonic jet. The use of O.P. grade nitrogen instead of prepurified nitrogen was investigated in a few experiments and found to lead to lower atom concentrations.

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NOMENCLATURE[†]Roman

a	number of moles of nitric oxide (NO)
Å	Angstrom unit (10^{-8} cm)
b	number of moles of $\text{NO}_2 + \text{N}_2\text{O}_4$
c_i	mass fraction of species i ($i = 1, 2, \dots$)
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
d	diameter of probe
D	Fick binary diffusion coefficient
h	Planck's constant
I	light intensity
k	rate constant
k_{wall}	effective first order rate constant for heterogeneous atom decay
$^{\circ}\text{K}$	degrees Kelvin
K_p	equilibrium constant
M	molecular weight
n	number density
\dot{n}	number flux
\underline{N}	normality
N_2^*	excited nitrogen molecule capable of decomposing NO beyond light titration end point
N_2^{**}	excited nitrogen molecule capable of decomposing NO before light titration end point

[†] Symbols describing the electronic state of atoms or molecules are not included in this listing but can be found in any standard reference in the field of spectroscopy, e.g., G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Sections I-3 and V-1. Second Edition, D. Van Nostrand Inc., New York, 1950. A. G. Gaydon, The Spectroscopy of Flames, Chapter IV. John Wiley and Sons, Inc., New York, 1957.

NOMENCLATURE (CONT'D)

N_2'	excited nitrogen molecule capable of decomposing NH_3
Nu_D	Nusselt number (dimensionless mass transfer coefficient)
P	pressure
Pe	Peclet number
r	$[S]/[He]$ in probe supply line
r'	$[S]/[He]$ into reaction zone
R	universal gas constant
s	distance along body surface
S	scavenger gas
t	time
T	absolute temperature
u	local gas velocity
v	vibrational quantum number
V	volume
x	distance in axial direction
X_i	mole fraction of species i
X	number of moles of gas

Greek

α	fraction dissociated
α_T	thermal diffusion factor
γ	recombination coefficient
δ	external diffusion boundary layer thickness
Δ	shock stand-off (detachment) distance
μ	dynamic viscosity
ρ	gas density
σ	molecular diameter (hard sphere model)
ν	frequency

NOMENCLATURE (CONT'D)Subscripts

d	downstream
e	just outside external boundary layer
exit	at scavenger probe exit
ln	logarithmic mean
mix	mixture
probe	through scavenger probe
r	recombination
Sc	scavenger gas
s	just behind normal shock
u	upstream
wall	pertaining to heterogeneous reaction

Superscripts

*	excited species
**	excited species
'	excited species

Miscellaneous

d	ordinary differential operator
exp	exponential function; $\exp x \equiv e^x$
grad	gradient operator
:	proportionality sign
.	complex
$\overline{(\quad)}$	average value of ()
[]	concentration (mole/cc)

I. INTRODUCTION AND OBJECTIVES

In previous reports experiments using catalytic probe methods to determine local atom and excited species concentrations in a supersonic stream of electrically discharged nitrogen ("active nitrogen") were described.^{1,2} Preliminary experiments using chemical methods also have been discussed there. A nonequilibrium plasma jet device was used to generate the active nitrogen.³ In this facility the products of a "high" pressure (usually above 20 mm Hg) continuous glow discharge were expanded through a converging-diverging nozzle shaped electrode into an evacuated test section. The jet so produced contained atoms and excited molecules in concentrations far in excess of the corresponding equilibrium concentration at the prevailing translational static temperatures of approximately 300°K. A schematic diagram of the electrode configuration is shown in Fig. 1.

In general, every current technique for quantitative determination of active species in a discharged gas stream has its limitations, and no single uncontested calibration standard is available. It is therefore desirable to develop several independent techniques based on distinct physicochemical principles and to correlate the results. To this end a "chemical scavenger probe" was developed which, like the catalytic probe method, allows measurement of local active species concentrations. The chemical scavenger probe is, in general, a device which samples a gas stream containing active unstable species (atoms, free radicals and excited species) and in which the sampled gas reacts rapidly with a "scavenger" gas. From the amount of reaction the concentration of the unstable species can be calculated. In the active nitrogen case there are reactions due solely to atoms and others due to atoms and excited molecules or excited molecules alone (see Section II). Chemical methods therefore have a greater specificity than the usual catalytic probe methods. They are, however, usually insensitive to molecules with a low degree of excitation. If present in large numbers such molecules may however contribute considerably to the total energy carried by the activated gas[†] and to the catalytic probe measurements.

[†]For example, it may be estimated from the work of Kaufman, Kelso⁴ and Dressler⁵ that a stream of active nitrogen, produced by a microwave discharge in a conventional flow system in the 1 mm Hg pressure range, carries about as much energy in the form of molecular nitrogen in the first vibrationally excited state of the ground electronic state as in the form of potential energy of recombination of atoms. Yet these vibrationally excited molecules are chemically inert, i.e., no reactivity due to them has been observed.

In this report experiments with the chemical scavenger probe at one discharge power output are described and the technique and results obtained are discussed. It is hoped that in the future, experiments can be undertaken at higher power levels and it is especially intended that at such time a direct comparison between the catalytic and chemical techniques will be made. In fact, a direct comparison between scavenger probe and thermal detector measurements will make possible a systematic study of the contribution of excited species to gas/solid energy transfer rates. It seems, moreover, desirable to further improve these techniques and to apply them to gases other than nitrogen for which they should have equal validity.

In Section II of this report the chemistry of active nitrogen is discussed. It is concluded that in view of the results obtained in conventional flow systems C_2H_4 , NH_3 and NO were appropriate gases for measuring atom or excited molecule concentrations with the scavenger probe. Some of the results of the present study are also discussed in this section.

In Section III the scavenger probe is described in detail. The sampling procedure and related flow phenomena are discussed as are pressure and temperature conditions and chemiluminescence inside the probe.

Section IV gives the experimental details.

Section V discusses the accuracy of the scavenger probe technique, i.e., the extent to which recombination and de-excitation could make the probe measurements systematically indicate a lower mole fraction of active species than actually existed in the free jet. It is concluded that the inferred mole fraction of atoms was not measurably different from that existing in the free jet. In contrast, the inferred mole fraction of excited molecules can conceivably have been lower than in the free jet. In this connection, more basic information on the nature of the excited molecules involved as well as data on collisional and radiative lifetimes are needed. Available information in this field is discussed.

In Section VI the observed extent of each reaction inside the scavenger probe is interpreted; the relative concentration of atoms and excited molecules and the amount of energy carried by each of these forms of active species are estimated.

II. A REVIEW OF THE CHEMISTRY OF ACTIVE NITROGEN

Several laboratories have recently reported on the chemistry of active nitrogen in conventional, Wood-Bonhoeffer type, flow systems.[†] Condensed (internal electrodes) as well as electrodeless discharges of the microwave and radiofrequency type have most commonly been used. A number of review articles have appeared.^{6,7}

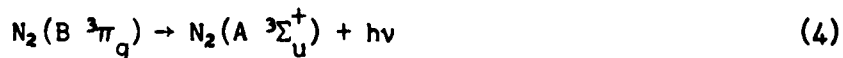
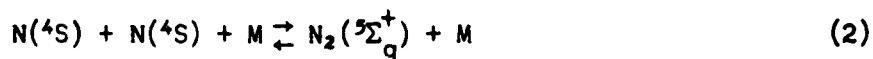
1. Composition and Chemiluminescence

Mass spectrometric investigations of active nitrogen detected only the production of ground state, 4S , atoms when a microwave discharge was used,^{8,8a} whereas a condensed discharge also produced excited molecules.⁹ The presence of ground state atoms was also demonstrated by electron spin resonance spectroscopy.^{10,11} Tanaka, et.al.¹² using a condensed discharge showed by vacuum uv absorption spectrophotometry that 2D and 2P atoms were also present, but in concentrations approximately 500 times less than that of ground state atoms. These observations were made with low pressure (0.1 - 10 mm Hg) discharges. Noxon¹³ showed that the concentration of 2P atoms increases rapidly with pressure and is about equal to 4S atoms at 1 atmosphere.

Mass spectrometric study also showed that the recombination of atoms is responsible for the emission of the yellow-orange Lewis-Rayleigh nitrogen afterglow, the intensity of which follows the equation⁸

$$I = \frac{d[h\nu]}{dt} = k[N]^2 [M] \quad (1)$$

This visible light emission is described by the mechanism⁸



The collision between $N_2(^5\Sigma_g^+)$ and M also leads to formation of the $Y\ ^3\Sigma_u^-$, $^3\Delta_u$ and a $^1\Pi_g$ states of nitrogen.¹⁴ Other nitrogen afterglows have been observed as well.^{15,16} Part of the decay of nitrogen atoms thus leads to the production of highly energetic

[†]Linear flow rates in such systems are of the order of 1 - 10 m/sec.

excited molecules and even ions.^{15,17}

2. The Reaction with Ethylene

A large number of chemical reactions in which active nitrogen participates have been studied. The reaction with ethylene yields HCN. Above a certain ethylene flow rate the flow of HCN produced remains constant; i.e., an HCN production plateau is reached. The appearance of a plateau which is independent of scavenger flow rate seems only possible when the scavenging reaction is fast compared to atom recombination, or in the case of excited molecule reactions, fast compared to de-excitation. Using spherical reaction vessels, the HCN plateau was found to be temperature independent from 520 to at least 720°K.¹⁸ Lower temperatures resulted in lower HCN flows¹⁹ at equal ethylene flows. However, when a straight reaction tube was used no temperature dependence of the HCN plateau was observed between 310°K and 710°K.²² Analysis of the products of the active nitrogen-ethylene reaction under conditions that both ethylene and nitrogen atoms were completely destroyed showed that 95 percent of the N in the reaction products was in the form of HCN and the remainder mainly in form of (CN)₂.²⁰ Methane, ethane and acetylene were also formed. The amount of (CN)₂ decreased with increasing ethylene flows. Similar results have been obtained by other workers.^{21,22} The temperature independent plateau of HCN has been considered as corresponding to the N-atom flow.^{18,22} There is much evidence to support this view. The maximum HCN production from ethylene is essentially the same as that obtained from a large number of reactants such as ethane,[†] propane, n-butane, isobutane, but-2-ene, cyclopentane, methyl- and dimethylacetylene, methylchloride,^{18,22} and also corresponds to the maximum O-atom production in the reaction with O₂²³ and the extent of reaction with NO₂.¹⁸ The limiting yields of HCN also have been reported to agree reasonably well with Wrede gauge measurements.²⁴

The reaction mechanism of the HCN formation has been postulated to be^{16,21}



[†]There is good evidence that at 360°K, although not at 670°K, the reaction with ethane is initiated by the same excited state of N₂ that is responsible for the reaction with NH₃ (see below).²⁵

To explain the lower limiting yield of HCN at lower temperatures in spherical reaction vessels, it has been postulated that the complex $N.C_2H_4$ has a relatively long lifetime and that its decomposition requires an activation energy. Under these circumstances ethylene can bring about homogeneous catalyzed recombination of N atoms by reaction (5) followed by^{19,26}



If the occurrence of reaction (8) is the correct explanation of the temperature dependence then the absence of temperature dependence of the HCN plateau found when using straight reaction tubes, i.e. the apparent occurrence of (8) to a negligible extent, has to be explained. Under these circumstances better mixing occurred than when spherical reaction vessels were used; hence, more efficient mixing could be a reason for the apparent absence of (8) at lower temperatures. Another explanation would be the following. In order for both reactions (5) and (6) to be spin allowed, a change in spin has to occur during the lifetime of the $N.C_2H_4$ complex.²⁰ Since the straight tubes used were considerably smaller in diameter than the spherical vessels, wall reactions could be more important in inducing the spin transition when the former were used. It is possible that a spin-allowed transfer reaction^{27,28,29} with the wall occurred which led to the change of the spin of the complex from $3/2$ to $1/2$, simultaneously causing the formation of a triplet state on the wall. The walls could thus catalyze the decomposition of the complex. A similar wall induced transition has been postulated to explain the NBr chemiluminescence in the active nitrogen-bromine reaction.³⁰

3. The Reaction with NH_3

The production of HCN from ethylene thus seems to be due to reaction of N-atoms. Active nitrogen from a condensed discharge also destroys ammonia; the only major products of this reaction are N_2 and H_2 .^{31,32,33} There is convincing evidence that the destruction of NH_3 is due to reaction of excited molecules and does not involve atoms; i.e., the reaction $N + NH_3$ is undetectably slow. This evidence may be summarized as follows. Active nitrogen from a microwave discharge does not decompose NH_3 to a measurable extent,^{34,35} nor does the concentration of atoms from it, as measured by mass spectrometry,³⁵ decrease to a measurable extent upon addition of NH_3 . Atoms are present in active nitrogen from both microwave and condensed discharges, but only in the latter is there a mass spectrometrically measurable amount of other species.^{8,9} The

reaction with hydrocarbons leads to a short reaction flame and the extinction of the nitrogen afterglow. Ammonia even in large excess does not extinguish the afterglow and the afterglow spectrum remains of normal appearance, although the intensity is reduced.^{34,35} The quenching must be due to reaction of NH_3 with excited molecules emitters (or precursors of emitters) of the afterglow. It has been shown^{19,36,37} that outside the discharge the species capable of destroying NH_3 is formed by homogeneous recombination of N-atoms, i.e., by the decay of the species capable of producing HCN from ethylene. Since the reaction $\text{N} + \text{NH}_3 \rightarrow \text{NH} + \text{NH}_2$ is endothermic by 19 Kcal/mole and the process $\text{N} + \text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2 + \text{H}$ is spin forbidden, it is not surprising that the reaction between atomic nitrogen and ammonia is undetectably slow.³⁵

The "absence" of NH_3 destruction in microwave discharge experiments may be attributed to the low atom concentrations. A microwave discharge gives about 1 percent dissociation, an order of magnitude less than usually obtained by condensed discharges. The decay of atoms leads to excited molecules capable of destroying NH_3 and some NH_3 destruction must occur. The production of very small amounts of H_2 from NH_3 has indeed been observed in microwave discharge experiments.³⁴

Freeman and Winkler³¹ showed that, at about 340°K, an NH_3 consumption plateau is reached; i.e., increase of NH_3 flow above a certain value does not lead to further destruction of NH_3 . This plateau is thus a measure for the concentration of excited molecules present. The activity of active nitrogen as measured by the NH_3 destruction plateau was, in the condensed discharge work, never more than 1/5th of the maximum HCN production under identical conditions.^{22,31} At temperatures above about 620°K and at 268°K, increasing the amount of NH_3 led to increasing amounts of NH_3 destruction and no destruction plateau was observed. Freeman and Winkler showed that this is probably due to secondary hydrogen atom attack rather than an increased reactivity of active nitrogen, since hydrogen atoms were shown to be unreactive towards NH_3 at 304°K, but reaction between hydrogen atoms and NH_3 did occur at those temperatures where the active nitrogen reaction led to destruction beyond the plateau value.

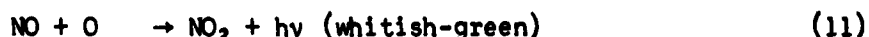
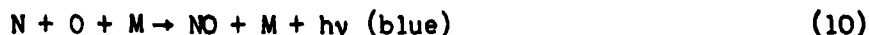
4. NO Light Titration and Total NO Decomposition

Another method used in several laboratories to measure the nitrogen atom flow makes use of the very fast reaction⁴⁰



The NO destruction plateau has been considered as corresponding to the N-atom flow.³⁴

A variant of this method is provided by the NO light titration technique,^{41,42} which is based upon the occurrence of the relatively slow light emitting reactions



When NO is mixed with active nitrogen and the NO flow is less than the N-atom flow, a blue chemiluminescence fills the reaction tube. At equal flow no light emission is seen and when the NO flow is in excess a whitish-green glow is emitted. In a system with good mixing these transitions are very sharp. Only a few percent of the NO added beyond the titration end point is consumed,⁴³ since (11) and



are followed by the much faster reaction⁴⁴



The plateau of NO destruction has been found to be independent of temperature from room temperature up to at least 670°K.¹⁸ In the following Section (II-5) the results obtained by the NO light titration and the NO decomposition plateau are compared.

5. Contribution of Excited Molecules to the NO Reaction and Comparison between the Ethylene and NO Reaction

Comparison studies of the NO destruction and temperature independent HCN production plateaus under the same conditions have been reported.^{18,22,45} At all pressures investigated the former gave higher values ranging from about 40 percent higher at 1 mm Hg to 140 percent at 16 mm Hg. It was found that the NO/HCN ratio did not change appreciably with atom concentration at a given pressure or with the type of discharge used (microwave or condensed) but did change with decay time. Since, as discussed, the temperature independent HCN production plateaus from ethylene agree with a number of other chemical methods for N-atom determination it has been suggested²² that the higher atomic nitrogen concentration indicated by the NO reaction is in fact due to participation of excited molecules in the NO reaction, which could also explain the dependence of the ratio of NO and HCN plateaus on decay time. In other words, an additional reaction



is assumed. Observations on the decay of N-atoms^{22,39} also suggest that the NO light titration gives too high a value for the N-atom concentration.

It was moreover found, at 2.5 mm Hg, that although the NO titration and NO destruction plateau gave the same values at low atom concentrations, at high atom concentrations from a condensed discharge the titration technique gave values 10 to 20 percent lower than those indicated by the NO consumption plateau.²² Although this rather small difference may possibly be considered trivial, a more striking result was obtained in the present work at higher pressures (Section VI-1), where the maximum amount of NO consumption was found to be 2.1 times as large as the NO light titration flow rate. To explain this discrepancy we again postulate destruction of NO by excited nitrogen molecules



The light titration technique indicates the point at which all N-atoms are destroyed, but part of the NO added beyond that point will be destroyed by (14a). Since (14a) will also occur simultaneously with (9), whether or not (14a) will falsify the gas phase titration to an appreciable extent as a measure for the N-atom flow depends on the ratio $k_9[\text{N}]/(k_{14a}[\text{N}_2^*])$. In the present work the amount of $[\text{N}]$ and $[\text{N}_2^*]$ was found to be of the same order. No direct measurements of k_{14} are available but (11) has to be competitive with (14a) in order for the whitish-green glow to occur when NO is added beyond the light titration end point, at which point all NO is destroyed and one O-atom is produced for each NO consumed.^{46,47} Hence k_{11} and k_{14a} will be of the same order of magnitude. Measurements of k_9 and k_{11} gave $k_9 = 2 \times 10^{-11}$ cc molecule⁻¹ sec⁻¹ (Ref. 48, 49, 50); $k_{11} = 6.5 \times 10^{-17}$ cc molecule⁻¹ sec⁻¹ (Ref. 51). Hence it appears highly unlikely that (14a) could cause a measurable falsification of the NO light titration.

If, as appears quite possible, the conclusion of Wright et.al.²² that the NO consumption at the light titration end point is partly due to excited molecule reactivity is correct, then it seems that two different excited molecules are involved in the NO reaction, N_2^{**} which reacts with a rate constant comparable to that of the N-atom reaction,[†] and N_2^* which reacts with a rate constant several orders of magnitude lower. Two observations should be made, however, on the agreement found by Winkler's group between HCN formation plateaus, the O-atom production from O_2 , and

[†]A recent study⁴⁵ using labelled NO rules out $\text{NO} + \text{N}_2^{**} \rightarrow \text{N} + \text{O} + \text{N}_2$ as an elementary reaction of similar rate as (9). However, an indirect process leading to NO decomposition remains a possibility.

the extent of reaction with NO_2 . First, since at the NO light titration end point one O-atom is produced for each NO molecule consumed,^{46,47} it seems contradictory that, in microwave discharge work, it was found that the maximum amount of HCN formation is equal to the maximum amount of O-atom formation from O_2 , but lower than the maximum amount of NO destruction,²³ and by inference lower than the NO light titration.²² The reaction with O_2 is given by^{23,40,48}



The NO formed will then react with N according to (9) and, if present, with N_2^{**} according to (14), both leading to further O-atom formation. At the temperatures where these observations were made, reaction (9) is about three orders of magnitude faster than (15).^{23,48,49} Hence, in a system where the NO light titration and HCN formation plateau do not agree it is not, a priori, understandable why the latter agrees with the formation of O-atoms from O_2 . Secondly, Clyne and Thrush,⁴⁶ using a radiofrequency discharge, found a NO(titration)/NO (destruction) ratio of 1.2 independent of pressure from 1.3 to 6.3 mm Hg. In the upper part of this range these values seriously disagree with the NO(titration)/HCN(destruction) values reported by Winkler's group,^{18,22} who found the latter ratio to be pressure dependent in the same pressure region. The agreement between HCN formation and NO_2 destruction¹⁸ may therefore have been fortuitous.

6. Summary

In the light of these recent results in the field of active nitrogen reactions, it appeared useful to study several active nitrogen reactions inside the chemical scavenger probe to arrive at active species concentrations in the supersonic jet. From the previous discussion it would seem that the HCN formation from ethylene and the NO light titration give a lower and upper limit, respectively, for the N-atom concentration. It is quite possible that some excited molecule N_2^{**} is responsible for part of the activity indicated by the NO light titration. The HCN formation involves more than one step and the extent of reaction has been shown to depend on flow conditions. This is a somewhat undesirable aspect in the adaptation of this reaction to the flow system used in this work, where conditions are quite different from previous conventional flow system studies. A difference between NO titration and NO consumption data, and in the present work a large difference was shown to exist, is a measure of $[\text{N}_2^*]$. Finally, NH_3 does not measurably react with N-atoms and its consumption is another measure of excited molecule concentration. A discussion of the

nature of the excited nitrogen molecules involved in these reactions is given in Sections V-6 and V-7.

III. CHEMICAL SCAVENGER PROBE

In view of the discussed specific reactions of nitrogen atoms and excited nitrogen molecules, a chemical scavenger probe was developed to systematically study these reactions in active nitrogen from a supersonic jet. The purpose of the experiments was to determine local atom and excited molecule concentrations. By doing this, one simultaneously investigates the relation of these reactions to each other with an active nitrogen source different from that used in previous chemical studies (Wood's tube or electrodeless discharge). Such a comparison is of interest because of the discrepancy between the results obtained from different type discharges. A full discussion of the conditions to which the probe had to adhere to accurately sample the stream is given in Section V. A chemical scavenger probe of different design and which was used to measure atom and free radical concentrations in burner flames has simultaneously been developed by Fristrom and co-workers.⁵²

It was considered undesirable to operate with high velocities inside the probe since this would have caused trapping problems and extended reaction zones. A detached shock inlet probe⁵³ was therefore designed which consisted of a 30 mm outer diameter quartz tube (wall thickness 2 mm) with a 90° angle (Fig. 2). The 8 cm long vertical section, the probe head, was partly blanked off, leaving an 8 mm diameter entrance orifice through which the active nitrogen jet was sampled by the probe. Directly behind the probe entrance orifice (Fig. 2) there was a 1 mm width annular opening through which the secondary gas, consisting of a helium-scavenger gas mixture, was introduced. The helium served as a coolant and also allowed measurement of the actual scavenger gas flow rate through the probe as discussed in Section IV-3. The downstream portion of the 50 cm long horizontal section of the probe was brought outside the wind tunnel test section through a vacuum-tight O-ring connection which, together with an asbestos sleeve contained within a brass collar whose position could be controlled, served to accurately center the probe head above the active nitrogen jet. The horizontal section ended in a 29/42 ground joint through which the probe was connected to a pyrex gas flow and analysis system.

The flat face of this probe head thus had a considerably larger diameter than the jet; the diameter of the latter was approximately equal to the nozzle exit diameter of 1.36 cm. The jet was stagnated by the scavenger probe and filled the test

section diffusely downstream of the probe. The part of the test section in which the probe was placed consisted of a stainless steel cross with viewing ports. The rectangular center duct of the cross, in the center of which the nozzle exit (Fig. 1) was located, was 6 x 12 cm. The actual portion of the jet sampled did not correspond to the 8 mm diameter of the probe opening itself since, in practice, the mass flow rate through the probe was maintained at a value smaller than the product of the free stream mass velocity and projected inlet area. Thus, using the observed N_2 flow rates in the probe (Table I) the probe was sampling the central 3.4 percent of the jet. The diameter of the stream tube being sampled was then calculated to be about 30 percent[†] of the inlet diameter of the probe.

The probe was placed about 5 mm downstream of the nozzle exit and centered by visual observation of the nitrogen afterglow inside the probe. The probe was considered properly centered when the afterglow filled the probe head. Small deviations from the centered position resulted in an unequal filling of the probe head; i.e., a beam of afterglow radiation directed against a portion of the probe walls. Once the probe was centered the positioning device held it firmly in place and no day to day adjustments were necessary. During the centering operation the secondary gas used was helium without added titrant.

The probe walls were poisoned with phosphoric acid. Under these circumstances, with only helium being used as the secondary gas, a bright afterglow filled the entire probe and extended well beyond the 29/42 joint. The upstream part of this glow was yellow colored but further downstream the color changed to pink-violet. The yellow glow was somewhat more pale than the Lewis-Rayleigh nitrogen afterglow at lower pressures. The pink-violet glow may be similar to the pink afterglows discussed by Beale, Broida and Young;¹⁵ however, no spectral study of the afterglows was made in this work. In preliminary experiments no wall poisoning was used and only a very faint afterglow was seen in the probe head, which indicated that most N-atoms recombined on the walls without light emission rather than homogeneously with light emission. This was somewhat unexpected since it was originally assumed that the helium would prevent a large fraction of the nitrogen atoms from reaching the walls in at least the inlet region of the probe head. This as well as the spilling of secondary gas out of the probe (see below) was indicative of a complicated flow pattern in the probe head. Small amounts of water added to the secondary or primary gas were used

[†] based on the free stream mass flow per unit area calculated from the total mass flow rate through the discharge and the geometric nozzle exit area.

in some preliminary experiments. Water vapor has been used as an efficient wall poison in a conventional pyrex flow system.³⁶ If the water vapor went through the probe for some time before the discharge was struck, an afterglow appeared which was less bright than when phosphoric acid was used and always faded after a few minutes. The same observation was made on an unpoisoned probe which had been exposed to the atmosphere shortly before the discharge was struck.

A 0.25 inch stainless steel tube could be moved along the center of the horizontal part of the scavenger probe through a vacuum tight O-ring junction (Fig. 2). It contained the leads of a chromel-alumel thermocouple and was also connected to a pressure gauge. The tube was closed at the end by a piece of quartz tubing which had a small hole downstream from the thermocouple junction. The quartz served to hinder direct recombination or de-excitation on the junction. Pressure (P) and temperature (T) were measured at the 90° bend in the scavenger probe before and after the experiments. While the gas samples were taken the P,T-probe was drawn out of the gas flow path. The measured temperature depended somewhat on the radial positioning of the thermocouple and was at a "reaction temperature" (see below) of 503°K, some 20° lower near the walls of the probe. Downstream from the 90° bend the temperature dropped rapidly to room temperature. Under the reaction conditions used in this work the pressure drop along the horizontal part of the probe was less than 0.05 mm Hg. Probe temperature and pressure did not show any dependence on the actual reaction studied. As judged by the extent of the violet reaction flame, the ethylene reaction came to completion in the probe head. The much faster reaction with NO also led to the formation of the titration glows in this region. The NH₃ reaction could not be followed by the appearance of a reaction flame but since the reaction of N₂' with NH₃ and N with ethylene have numerically close rate constants³⁶ it is likely that most of this reaction also occurred in the probe head (further details on the probe reactions are given in Section VI).

The active nitrogen sucked in at the probe entrance orifice was presumably at a temperature close to that of the shocked gas, i.e., of the order of 900°K for the conditions studied. The premixed secondary and titrant gas mixture entered the probe at a temperature somewhat above room temperature since some heat must have been absorbed from the inlet region of the probe which was heated by the shocked gas.[†] Reaction occurred when primary and secondary gas mixed. The temperature at the 90°

[†] It was for this reason that quartz rather than pyrex was used as the scavenger probe construction material. Temperatures in the range of 1200 - 1400°K could have been expected for high discharge current experiments.

bend in the probe thus represented an average reaction temperature[†] but reaction actually occurred over a range of temperatures. Wherever in this report the words "reaction temperature" or "probe temperature" are used it is this average measured temperature which is meant.

Table I gives a summary of the probe and discharge conditions in the actual experiments. It should be noted that although the secondary gas was introduced inside the probe, only about 18.8 percent of the helium was actually flowing through the probe; the rest spilled out.[‡] Nevertheless, adequate nitrogen sample sizes were obtained in this way and, in addition, the secondary gas spillage served to blanket the interior and exterior surfaces of the quartz probe head, thereby minimizing any thermal problems which might have been associated with direct impingement of the active nitrogen jet. The amounts of nitrogen and helium flowing through the probe also depended critically on the probe position. In some preliminary experiments in which the probe superficially appeared to be in the same position as for the experiments of Table I, the nitrogen flow rate through the probe was 33 percent higher, the helium flow rate 38 percent lower, and the probe temperature 120° higher than for the experiments of Table I. For these experiments the total flow and discharge conditions were the same as for the experiments of Table I and the probe pressure was 17.8 mm Hg.

The effect of closing off the helium stream was investigated in another preliminary series at the same discharge and total flow conditions of the experiments of Table I. With the helium flowing 18.2 percent of it went through the probe. Shutting it off increased the percentage of the total N₂ flow going through the probe from 3.3 to 5.6 percent, while the probe temperature rose from 475 to 565°K and the probe pressure dropped from 17.9 to 16.2 mm Hg for a fixed position of the probe flow system needle valve.

[†] probably a somewhat low average since most of the reaction actually occurred upstream from the point of measurement.

[‡] This made the probe inlet "wall-less". Possible effects of scavenger gas spillage on the accuracy of the probe measurements are discussed in Section VI-5 and Appendix D.

IV. EXPERIMENTAL

1. Operating Conditions

An all-copper axisymmetric nozzle of exit diameter 1.36 cm, throat diameter 0.657 cm was used. Assuming $c_p/c_v = 1.4$ the exit Mach number for this nozzle is about 3. The electrode configuration used is shown in Fig. 1. The nozzle was the anode in all experiments. The distance between the tip of the coaxial rod electrode and the nozzle entrance was 6.8 cm. The diameter of the undisturbed jet, *i.e.*, the jet upstream of the scavenger probe, was about equal to that of the nozzle exit diameter. For all experiments the pressure was 38.5 ± 0.5 mm Hg in the discharge chamber and 1.00 ± 0.02 mm Hg in the test section. Further flow and discharge conditions are summarized in Table I.

2. Materials

Airco prepurified nitrogen, U.S. welding helium, Matheson C.P. ethylene and anhydrous ammonia were used without further purification. Matheson nitric oxide was freed of NO_2 by passage through a column of 8-20 mesh Fisher Caroxite. The oil manometers were filled with Dow-Corning 702 silicone oil. Fisher reagent grade potassium hydroxide, potassium iodide, ammonium hydroxide, silver nitrate, potassium cyanide, sulphuric acid, hydrazine sulphate, para-dimethylaminobenzaldehyde, phosphoric acid and U.S.I. ethyl alcohol were used.

3. Flow System

A Stokes model 1712 mechanical booster vacuum pump combination of nominal capacity 2500 cfm was used. Pressures were measured with Wallace and Tiernan (Bourdon type) absolute pressure gauges. Flow rates of nitrogen and helium were measured with calibrated sonic orifice meters. For the titrant gas a calibrated rotameter was used. A thorough mixing of helium and titrant gas was obtained by passing the combined flow of these gases through a column packed with 1/4 inch Berl saddles before introduction into the sampling probe.

The scavenger probe flow system used is shown schematically in Fig. 3. The effluent probe gases consisted of N_2 , He, unreacted titrant and reaction products. The condensibles could be trapped by two consecutive cold traps and thence transferred in the conventional manner to a number of known volumes for PV measurement, using a silicone oil filled manometer, or to a demountable analysis flask. Liquid air traps

were used, and for the NO experiments they were pumped down. A small coil of cobalt plated platinum wire was placed ahead of the traps to recombine O-atoms formed in the reaction with NO, which prevented ozone formation in the traps. The whole flow system, downstream from the sonic orifice meters in the N₂ and He lines, was pumped out for periods of at least 16 hours prior to an experiment. Measurements were made after discharge stabilization periods of at least half an hour.

The flow rates of N₂ and He through the probe were calculated from the N₂/He ratio as determined by an effusion analyzer (see below) and the combined N₂ + He flow as determined by collection through a sonic orifice into a 239 liter volume. The flow rate of titrant through the probe before destruction in an active nitrogen experiment could then be calculated directly from the known titrant gas-helium ratio. The difference between this flow rate and the one determined by actual trapping gave the amount of titrant destroyed by the active nitrogen. The titrant gas-helium ratio was determined in blank experiments with the active nitrogen stream shut off.

The effusion analyzer was submerged in a constant temperature water bath. It consisted of a fixed (~250 cc) volume, out of which gas could effuse through a small hole into a continuously evacuated line. The pressure drop from a constant initial pressure in the fixed volume after a certain time interval (30 minutes) was calibrated in terms of the N₂/He ratio. The effusion analyzer was filled with the aid of a Toepler pump. The gas analyzed by the effusion analyzer contained, of course, the uncondensable reaction products, i.e., N₂ and H₂ in the NH₃ reaction,³¹ small amounts of H₂ and CH₄ in the ethylene reaction²⁰ and possibly some O₂ in the reaction with NO. The reaction products formed were however only a small fraction of the total N₂ + He flow through the probe and had an effect well within the limits of accuracy of the N₂/He ratio determinations (compare Table I).

Upstream from the 239 liter volume there was a needle valve with which the flow rate through the probe could be adjusted (Fig. 3). The pressure upstream P_u, and downstream P_d, from this "valve orifice" could be measured. With stopcock A open to the vacuum pump line the relation between P_u and P_d was such that the flow through the valve orifice was sonic. When stopcock A was turned so that the gas streamed into the previously evacuated calibrated 239 liter volume, the flow rate through the valve orifice remained the same as before, as long as the flow through it was sonic. Before P_d reached a value for which this condition was no longer fulfilled, stopcock A was turned back again to the pump line. Measurement of the pressure in the 239 liter vessel and of the collection time gave the flow rate. At the flow rates used,

the collection times were of the order of 1 to 5 minutes. Stopcock B allowed the vessel to be re-evacuated for succeeding measurements.

4. Ethylene Experiments

The reaction products of the ethylene reaction were distilled at temperatures equal to or less than 23°C (the melting point of solid CCl_4 , with which the traps were covered) into a removable analysis flask containing about 25 cc of frozen 1 N KOH solution. This solution was next partially melted by submerging the bottom part of the flask in hot water and the still solid HCN was then dissolved in it.[†] In this way polymerization of HCN was prevented. The KCN was then titrated by the Liebig-Deniges method⁵⁴ using standard 0.1 N AgNO_3 .

5. NH_3 Experiments

The amount of undestroyed NH_3 was analyzed either by PV measurement or by dissolving it into excess 0.1 N H_2SO_4 followed by back titration with 0.1 N KOH. Both methods agreed to within 2 percent. Hydrazine was analyzed for by the method of Freier and Resch.⁵⁵ Its production did not exceed 0.005 percent of the amount of NH_3 destroyed. These results confirm those of previous workers who showed that N_2 and H_2 were the only major reaction products.^{31,32,33}

6. NO Destruction Experiments

To determine the total amount of undecomposed NO present in the trapped products as NO and $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ a new method was developed. The trapped products of the NO reaction were transferred to a known volume V_1 and the pressure P_1 was measured[‡] at room temperature, from which X , the number of moles in V_1 , was calculated. The gas was then expanded into a second known volume V_2 which included V_1 and was approximately four times V_1 . The pressure was now P_2 and Y moles of gas were present. From these data and the equilibrium constant $K_p = (P_{\text{NO}_2})^2 / P_{\text{N}_2\text{O}_4}$, the amount of undecomposed NO was calculated in the following manner (for details see Appendix A).^{††} If a is the number of moles of NO and b the number of moles of $\text{NO}_2 + \text{N}_2\text{O}_4$, counted

[†] This method was suggested to us by Dr. A. N. Wright of Dr. C. A. Winkler's laboratory at McGill University.

[‡] The pressure P_1 was such that the partial pressure of $\text{NO}_2 + \text{N}_2\text{O}_4$ was less than 10 mm Hg.

^{††} The equilibrium data of Srivastava and Barua⁵⁶ were used, together with $\Delta H = 13.9$ Kcal mole⁻¹ (Ref. 57).

as NO_2 , per mole of NO , then $(a)(1 + b)$ is the equivalent amount of undecomposed NO . Defining further α_1 and α_2 as the fraction of N_2O_4 dissociated in volume V_1 and V_2 , respectively, and

$$Q \equiv \frac{4 P_1}{K_p} \left(\frac{Y - X}{X} \right)$$

we obtain

$$a(1 + b) = \frac{(1 - \alpha_1)Y + (1 - \alpha_2)X}{\alpha_2 - \alpha_1} \quad (\text{A})$$

in which

$$\alpha_2 = \alpha_1 \{ 1 + [\alpha_1 / (1 - \alpha_1)] Q \} \quad (\text{B})$$

and

$$\frac{\alpha_1}{1 - \alpha_1} = \frac{-1 + \{ [V_2 / (V_1 Q)] [Q + (V_2 / V_1) - 1] \}^{\frac{1}{2}}}{Q + (V_2 / V_1)} \quad (\text{C})$$

The method was checked by introducing known amounts of NO into the system followed by partial oxidation of the NO and agreement was found to be within 2 percent. The developed method involves admittedly considerable calculation but has the advantage of being experimentally faster than the conventional method of total oxidation of the trapped sample, followed by PV determination of the equivalent amount of NO as $\text{NO}_2 + \text{N}_2\text{O}_4$. For one experiment the equivalent amount of NO was determined both ways. The agreement was again better than 1 percent which also showed that less than one mole percent of the condensables could have been substances other than NO and NO_2 . The absence of N_2O in the reaction products is in agreement with the results of earlier workers.^{18,40} The PV measurements also yield directly the amount of non-oxidized NO in the sample since

$$a = \frac{(1 + \alpha_2)X - (1 + \alpha_1)Y}{\alpha_2 - \alpha_1} \quad (\text{D})$$

which makes it also applicable to the NO_2 titration of O-atoms by the clean-up method.⁵⁸

V. SAMPLING CONDITIONS, RECOMBINATION, AND DE-EXCITATION

To accurately measure local atom and excited molecule concentrations in the jet the probe had to fulfill the condition that the composition of the gas did not change due to the presence of the probe; i.e., the gas flow must be chemically "frozen" up to the point of reaction. As discussed in Section III, only a fraction of the free stream mass flux subtended by the probe inlet orifice found its way into the probe; the remainder flowed around it in an external, higher density, shock layer. It is then necessary to show that there existed a compatible range of operating conditions in which, ideally, recombination and de-excitation in the external shock layer and boundary layer were negligible and, at the same time, clean-up reactions in the probe were complete in a relatively few probe diameters. This can be done most simply by combining several experimental observations with a series of overly pessimistic order-of-magnitude calculations, as outlined below.

These calculations are based on an N atom concentration in the central part of the jet of 1.15 mole percent, the actually determined N₂ and He probe flow rates, the NO light titration end point probe flow rate, and an ethylene probe flow rate of 3.4×10^{-6} mole sec⁻¹ (compare Table I and Section VI). The probe pressure, temperature, and linear velocity used were also those determined in this work (Table I). The collision diameters used were: $\sigma_N = 2.7 \text{ \AA}$ (this value is about in the middle of a range of reasonable values;⁵⁹ $\sigma_{N_2} = 3.4 \text{ \AA}$ at 900 K, calculated from the Lennard-Jones potential parameters assembled in Ref.⁶⁰). Pressures and temperature behind the shock and at the outer edge of the external boundary layer (Fig. 4) were estimated from the observed discharge-to-test section pressure ratio (38.5 to 1) and the one-dimensional compressible flow relations⁵³ for a gas with $c_p/c_v = 1.4$. The free stream stagnation temperature, $T_\infty + \frac{1}{2}u_\infty^2/c_p$, was estimated to be about 900°K on the basis of previous noncatalytic thermometer measurements made in this laboratory.¹

1. Homogeneous Recombination in the Shock Layer

For a weakly dissociated gas the decay of atom mole fraction X_N across a shock layer of thickness Δ is governed by the expression^{†61}

$$\frac{X_{N,e}}{X_{N,s}} = \frac{1}{1 + X_{N,s} \int_0^\Delta [k_r n^2/u] dx} \quad (E)$$

[†] Subscript e = outer edge of boundary layer; subscript s = immediately behind shock.

where $u(x)$ is the streamwise velocity in the layer and n the total number density, i.e., the total number of atoms and molecules per cc (see Fig. 4).

Estimating the integral as $k_r n_e^2 \Delta / (\frac{1}{2} u_g)$ and inserting the value $k_r = 3 \times 10^{-31} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ (cf. Section VI-3) as a possible upper limit to the 3-body rate constant and $\Delta \sim 2 \text{ mm}$, it was calculated that, for the conditions of the present experiments, the atom mole fractions on either side of the shock layer should differ by something of the order of only a few parts in ten thousand.

2. Homogeneous Atom Recombination in the External Diffusion Boundary Layer

Strictly speaking, a stagnation point boundary layer (in the usual sense) did not exist at the nose of the probe owing to the presence of the 8 mm diameter sampling orifice. However, even in the absence of the sampling orifice in the stagnation region (see Fig. 4), one can show that a negligible amount of atom recombination would take place in the external boundary layer under the conditions of the present experiments. To do this one need only observe that the time to diffuse across such a boundary layer would be of the order of the reciprocal of the inviscid gas velocity gradient du_g/ds ; i.e., the reciprocal of the gas velocity gradient perpendicular to the jet axis established at the probe entrance,⁶² which in turn would be of the order of the free jet diameter[†] divided by the gas velocity behind the normal shock. Inserting this estimate into an expression of the same form as Eq. (E), it was calculated that the atom concentration on either side of the diffusion boundary layer would differ by something of the order of only a few parts per thousand.

3. Homogeneous Atom Recombination in the Probe Itself

From the net flow rates through the probe it is possible to estimate to what extent the atom concentration would decay in the absence of competing reactions over the 3 probe diameter distance (i.e., the length of the probe head) observed to be necessary to complete the scavenger reactions within the probe (compare Section V-5). Again, a relation of the form of Eq. (E) is appropriate, except the velocity u is taken to be a constant average value \bar{u} corresponding to the observed probe flow rates and pressure level. Using the more reasonable rate constant $k_r = 3 \times 10^{-32} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ (compare Section VI) at the lower temperature levels, it was calculated

[†] It has already been noted that the overall probe diameter exceeded the jet diameter. For this reason the jet diameter is the significant characteristic length in determining the velocity gradient.

that the X_N would at most drop to 0.67 of its original value within the observed mixing clean-up zone in the absence of clean-up reaction. Actually, the three-body loss mechanism was competing with the scavenger-N-atom clean-up reaction which went to completion in this zone. For the slowest scavenger reaction (*i.e.*, ethylene at the lowest flow rate used)[†] the scavenger reaction path removed atoms 8 times faster than the 3-body path within the probe. In view of the large possible error in the rate constant used for the $N + C_2H_4$ reaction, it may be argued that the difference in rate between the two paths is not significant. However, the HCN production was found to be independent of the ethylene flow rate over the range investigated (Table I and Fig. 9) which more convincingly demonstrates that the N-atom recombination (homogeneous and heterogeneous) was insignificant as means of removing N-atoms compared to the clean-up reaction in the region where both reactions competed. The decay of X_N in the absence of scavenger gas appears, moreover, considerably less than indicated by the above calculation since a bright nitrogen afterglow was observed in the probe more than 20 diameters downstream of the probe inlet. The latter two observations make it likely that, in practice, homogeneous atom recombination exerted no significant effect on the results.

4. Wall Losses Within the Probe

One can obtain an upper limit to the extent of heterogeneous atom decay by recombination within the probe assuming one-dimensional flow within the probe and neglecting any diffusional limitation on the rate. In this case the law for atom decay is

$$X_N/X_N(0) = \exp(-k_{\text{wall}} x/\bar{u}) \quad (F)$$

where the effective gas phase rate constant k_{wall} is related to the conventionally defined atom recombination coefficient γ as follows

$$k_{\text{wall}} = \left(\frac{8 R T_w}{\pi n_N} \right)^{\frac{1}{2}} \frac{\gamma}{d}$$

[†] - $d[N]/dt = k[N][C_2H_4]$; $k = 0.9(\pm 0.7) \times 10^{-13}$ cc mole⁻¹ sec⁻¹ (Refs. 36,63,64,65).
 - $d[N]/dt = k[N][NO]$; $k = 2 \times 10^{-11}$ cc mole⁻¹ sec⁻¹ (Refs. 48,49,50).

These direct determinations of the latter rate constant agree within experimental error which for the last two references quoted was ≤ 50 percent. Both reaction rate constants show only a small temperature dependence.

In the 3-diameter length experimentally required to complete the clean-up reactions (see below), one finds that the atom mole fraction would drop to 0.72 times its original value if the recombination coefficient for the poisoned quartz surface is estimated⁶⁷ as 3×10^{-4} and no reaction with the scavenger occurred. The visual observation that the afterglow intensity dropped only slowly when no scavenger was present again suggests that this estimate is overly pessimistic.

Moreover, wall losses should have been considerably smaller than this, since over most of the probe head the regions near the probe walls were apt to be much richer in scavenger gas and helium than the central region of the flow. Reaction with the scavenger gas would thus have prevented most of the N-atoms from reaching the wall, since even the rate of N-atom decay for the slowest scavenger reaction (compare Section V-3) is more than 10 times the corresponding rate for wall reactions in the probe head.

Particularly for this latter reason, heterogeneous recombination in the probe entrance orifice itself should have been negligible because of the secondary gas spillage. Even straightforward application of Eq. (F) would lead to the conclusion that the N-atom concentration decayed only a few parts in a thousand due to wall losses in the entrance orifice.

5. Completion of Scavenger Reactions in the Probe

Assuming instantaneous mixing and one-dimensional flow within the probe head, one can estimate the loss of N atoms due to the titrant reaction alone from the decay law

$$X_N/X_N(0) = \exp(-k\bar{n}_{sc} x/\bar{u}) \quad (G)$$

where \bar{n}_{sc} represents the prevailing average scavenger number density and k the rate constant of the N-atom/scavenger reaction. From the observed flow rates and pressure in the probe, it was calculated that the slowest reaction, i.e., ethylene at its lowest flow rate, would be 95 percent complete [$X_N/X_N(0) = 0.05$] in about 1.8 probe diameters. In 3 probe diameters X_N would have decayed to 0.8×10^{-2} its initial value. It was experimentally observed that the blue light emission typical of the N-atom ethylene reaction appeared through most of the probe head but not in the horizontal part of the probe. This suggests that the N-atom/ethylene reaction took about 2 to 3 probe diameters to be completed. Interestingly enough, calculations show that lengths of about this magnitude could also be required on the basis of mixing con-

siderations alone.[†] Even for the slowest atom clean-up reaction, i.e., $N + C_2H_4$, mixing within the probe head may therefore have played some role in determining the observed length of the reaction zone. If this were the case, it follows that mixing would play a more important role in the case of the $N + NO$ reaction, since the rate constant for the reaction $N + NO$ is two to three orders of magnitude greater than the corresponding rate constant for the reaction between N and C_2H_4 .

6. Nature and De-excitation of Excited Nitrogen Molecules Responsible for the NH_3 Decomposition

A large number of electronically excited states are known to exist in active nitrogen.[‡] All of these states have sufficient energy to decompose NH_3 . Bayes⁶⁸ has given evidence that NH_3 quenches the $A^3\Sigma$ state preferentially to the $^5\Sigma$, $B^3\Pi$ and $Y^3\Sigma$ states, and also showed that the $A^3\Sigma$ state is more likely to be responsible for the reaction with NH_3 than high vibrational levels of the ground state. The work of Dunford³⁷ also indicates that the $A^3\Sigma$ state is responsible for the reaction with NH_3 . Nevertheless, since NH_3 has been observed to quench the afterglow, some additional reaction with the $^5\Sigma$ state or an upper state of the afterglow emission seems to be necessary; there is good evidence¹⁴ that the $^5\Sigma$ state is quenched by NH_3 . Quenching does not necessarily lead to NH_3 destruction, however.

The more probable value for the radiative lifetime of the $A^3\Sigma$ state is of the order of 1 sec,^{13,69,70} and it has been estimated that more than 10^9 collisions^{††} with N_2 are required to bring about deactivation of this state.¹³ The total number of collisions with N_2 undergone by one $N_2(A^3\Sigma)$ molecule in 3 probe diameters is between 1×10^6 and 4×10^6 , depending on whether immediate mixing or no mixing with secondary gas is assumed; about 4×10^3 collisions would occur in the shock and external diffusion boundary layers and 10^5 collisions in the probe entrance orifice.^{‡‡}

[†] i.e., on the basis of the length required for a substance initially present only at the stream tube boundary to diffuse on a molecular level to an appreciable extent into the core flow. However, the NO trapping data (Appendix D) suggest that mixing rates within the probe head are considerably larger than those corresponding to molecular diffusion alone.

[‡] An energy level diagram of nitrogen⁷¹ is shown in Fig. 5.

^{††} This figure was obtained at room temperature and could conceivably have been lower at the higher temperatures of the present work. Such a temperature dependence has, for example, been observed in the quenching effectiveness of argon by mercury which is about 5 times higher at 1000°K than at room temperature.⁷² Also impurities may preferentially de-excite the $A^3\Sigma$ molecules.⁶⁹

^{‡‡} assuming N_2^1 to have the same collision diameter as N_2 . This is the same assumption as made by Noxon¹³ to calculate that $N_2(A^3\Sigma)$ could survive 10^9 collisions with N_2 .

The total time it took a gas parcel to travel from immediately behind the shock to the 90° bend in the probe was about 5×10^{-3} sec. Since the reactions $N_2^1 + NH_3$ and $N + C_2H_4$ have rate constants of similar magnitude,³⁶ it may be assumed that the reaction between N_2^1 and NH_3 was also completed within 3 probe diameters (cf. Section V-5). Hence it appears probable that negligible homogeneous de-excitation with N_2 or radiative decrease of $X_{N_2}(A^3\Sigma)$ occurred in the period necessary for clean up of the $A^3\Sigma$ molecules by NH_3 .[†] De-excitation by helium does not appear possible since the lowest triplet state of this atom is 19.72 ev above the ground state,⁶⁶ and the lowest excited singlet state lies even somewhat higher. This represents more energy than would be available from $A^3\Sigma$ or even higher excited N_2 molecules.

Little is known about the number of collisions with the walls required to deactivate $N_2(A^3\Sigma)$. The absence of the Vegard-Kaplan bands ($A^3\Sigma \rightarrow X^1\Sigma$) in the afterglow emission at low pressures has been attributed to wall deactivation of the $A^3\Sigma$ state.¹³ It is therefore possible that wall deactivation played a more important role than that calculated for wall recombination in Section V-4.

7. Nature and De-excitation of Excited Nitrogen Molecules Responsible for the NO Decomposition

Except for $A^3\Sigma$ ($v = 0,1$) all of the electronically excited states of nitrogen have energy in excess of 6.48 ev, the dissociation energy of NO.^{73†} There are, therefore, a priori, many possible states which could decompose NO. Ground state N_2 with $v \geq 27$ also has enough energy to decompose NO.⁷³ In the following, these excited states are discussed and it is concluded that metastable electronically excited molecules formed in the discharge are responsible for most of the observed reactivity. It is possible that the metastable state involved is again the $A^3\Sigma$ state, which should form a large fraction of the excited molecules present, since it is formed not only by direct recombination of atoms but is also the lower state for most commonly observed afterglows.

The state, N_2^{**} , which may be responsible for the difference between the NO light titration and the HCN production in a conventional flow system has recently been discussed by Wright et.al.²² The present discussion pertains to the state or states, N_2^* , which may be responsible for the difference between the NO destruction and NO light titration observed in the present work. Although much of the argument

[†] Additional $N_2(A^3\Sigma)$ may have been formed in the probe through atom recombination.

[‡] For an energy level diagram⁷¹ of NO see Fig. 6.

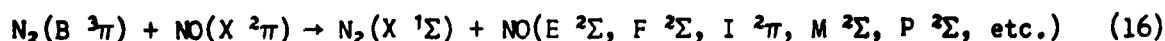
applies to either state, it is, as discussed in Section II-5, possible that different excited states are involved in these two reactions.

The $v = 27$ level of ground state N_2 has been observed⁷³ but it is not too likely that enough of such molecules are available to cause considerable NO decomposition.[†] Also relaxation of the highest vibrational levels probably occurs rapidly at the temperature of the discharge, the region behind the shock and the external diffusion boundary layer, since the vibrational quanta are of equal magnitude as translational quanta under these conditions and energy transfer therefore occurs readily.^{74‡} Vibrationally excited ground state molecules were also formed in the probe head by the reaction^{4,75}



The maximum energy that is available for vibrational excitation of the newly formed bond equals the exothermicity of the reaction, i.e., 3.28 eV corresponding to $v = 12$. This is insufficient to directly decompose NO.

Heath⁷¹ has shown that NO quenches the emission of the first positive group ($B \ ^3\pi \rightarrow A \ ^3\Sigma$) bands in high pressure air discharges and contributed this to one or more of the following reactions



All of these excited states of NO have energies above the dissociation limit of the ground state (Fig. 6 and Ref. 76) and the reactions appear to have a reasonable probability of occurring,⁷¹ i.e., for resonance transfer.⁷⁷ For the following reasons it appears unlikely, however, that reaction with $B \ ^3\pi$ state molecules contributed appreciably to the reactivity toward NO observed in this work (compare Section VI-1). The radiative lifetime of the $B \ ^3\pi$ state is of the order of 10^{-6} sec.^{13,70} The linear flow rate of the undisturbed jet was about 10^5 cm sec⁻¹. Hence, a gas parcel needed about 10^{-5} sec to travel from the nozzle throat to the shock front and

[†] Application of the Franck-Condon principle to the N_2 potential energy curves also shows that the $v = 27$ level is not favored to be populated by decay of electronically excited levels formed upon atom recombination.

[‡] Ground state molecules with $v = 1$ take about 5×10^6 collisions to relax at 900°K.¹⁰⁰

10^{-4} sec to get from there through the probe entrance orifice. The local $B\ ^3\pi$ concentration was therefore not determined by its concentration in the nozzle throat but by the local concentration of atoms which formed this state by radiationless collision induced transition from the $^5\Sigma$ state.^{8,14} This, however, means that the concentration of $B\ ^3\pi$ molecules could not exceed one half that of the recombined number of atoms which in itself was only a small fraction of the total number of atoms present (Section V-3). Moreover, it is likely that the recombination of more than 10 atoms are in fact needed for the emission of one first positive band light quantum^{13,78} in the pressure region of interest (18.8 mm Hg downstream from the shock), and even at higher pressures radiationless de-excitation of $B\ ^3\pi$ molecules by N_2 seems to be unimportant compared to the depopulation of this state by light emission.¹³ The present work, however, showed (Section VI-1) that the concentration of excited molecules is more than one half that of the atoms present. It therefore appears that the $B\ ^3\pi$ state cannot be the state that is responsible for most of the observed NO decomposition. Of the other states formed from the $^5\Sigma$ state the $\gamma\ ^3\Sigma$ and $^3\Delta$ states are the upper levels for fully allowed transitions and hence should have radiative lifetimes comparable to or shorter than that of the $B\ ^3\pi$ state. The metastable $a\ ^1\pi$ state also formed from the $^5\Sigma$ state has a longer lifetime,⁷⁹ but again atom recombination outside the discharge does not seem to be sufficient to account for most of the observed excited molecule reactivity.[†] The $^5\Sigma$ state, which is in equilibrium with ground state atoms, does not appear to be a likely major reactant either, since at 500°K its decomposition rate constant⁸ via[‡]



is probably comparable to that of the $N + NO$ reaction and at concentrations of $N_2(^5\Sigma)$ comparable to $[N]$, (-2) may well be faster than this reaction since $[M] \gg [NO]$ (compare Table I); the reaction of NO with N atoms is several orders of magnitude faster than the reaction with N_2^* (compare Section II). It thus appears that the N_2^* , responsible for the reaction with NO, is partly or mostly formed inside the discharge and that this N_2^* is a metastable state.

[†] The same would apply to any other excited state formed by atom recombination outside the discharge.

[‡] The activation energy of (-2) is in fact lower¹⁴ than indicated by Ref. 8.

It has been proposed that the $A^3\Sigma$ state could react with NO by the process²²



This process would have a high probability for resonance transfer. However, although $A^3\Sigma(v = 0,1)$ can survive more than 10^9 collisions, there is evidence that vibrational relaxation of the higher levels of this state requires many fewer collisions.¹³ The $v = 0,1$ levels of the A state have,^{80,81} however, less energy than $D(NO) = 6.48$ ev.

An alternate process by which $N_2(A^3\Sigma)$ could decompose NO has been postulated by analogy to the photosensitized decomposition⁸² of NO by Hg $6(^3P_1)$ which carries 4.86 ev of excitation energy, i.e., less than the $A^3\Sigma$ state (compare Fig. 6). This process has been explained by assuming the intermediate formation of a $NO(^4\Pi)$ molecule of long radiative lifetime.^{83,84} Like $NO(X^2\Pi)$, $NO(^4\Pi)$ correlates with ground state atoms.^{76,85} The analogous process in the active nitrogen reaction would be the spin allowed reaction



which would again have a high probability, since it also satisfies the Franck-Condon principle and the condition⁷⁷ that little energy would have to be changed or received from translation.^{†,‡} The $NO(^4\Pi)$ molecule could then collide with a second excited nitrogen molecule and decompose, or alternately could react by⁸³



or^{82,84}



[†] For the pertinent potential energy curves of N_2 , see, e.g., Heath⁷¹ and for NO, Fallon et.al.⁸⁵

[‡] A process similar to (18) but involving ground state vibrationally excited molecules would be spin forbidden and thus therefore not have to be further considered.

The latter reaction can be excluded since no N_2O formation was observed in the present study contrary to the photosensitized reaction.⁶⁴ Reactions (20) and (21) would thus lead to two NO molecules decomposed for every $\text{NO}(^4\pi)$ formed, which was not de-excited before reaction.

It is therefore possible that, as discussed for A $^3\Sigma$ state molecules in the reaction with NH_3 , little de-excitation before reaction occurred. On the other hand, the evidence for A $^3\Sigma$ as the excited state responsible for the reaction with NO is speculative and the observed reactivity could conceivably also be due to the metastable $a' ^1\Sigma$ or a $^1\pi$ state. The $a' ^1\Sigma$ state may have a radiative lifetime comparable to the A $^3\Sigma$ state;⁸⁶ the lifetime of the $a' ^1\pi$ state may be too short.^{16,79} Both states could decompose NO into ground state atoms in a spin allowed reaction similar to (14b), whereby the N_2 molecule ends up in the X $^1\Sigma$ state. In the absence of more information on the identity of N_2^* and its collisional and radiative lifetime, it is difficult to state anything definite at this time about the extent of its de-excitation before reaction with NO.

8. Conclusions

The foregoing considerations make it likely that the atom recombination before reaction would not cause the mole fraction of atoms to be appreciably lower than in the undisturbed jet. If the A $^3\Sigma$ state is indeed responsible for most of the observed reaction with NH_3 and NO, then it is probable that de-excitation before reaction was also not important. Especially for the NO reaction more basic information is needed, however, and the mole fraction of excited species as measured by the difference between the NO destruction and light titration could, therefore, have been lower than in the free jet.

VI. RESULTS AND DISCUSSION1. NO Light Titration and NO Decomposition

The results of the NO light titration experiments and the NO decomposition experiments have been summarized in Table I and are shown in Fig. 7. The NO light titration end point was seen as a series of blue and white-green flashes following each other in rapid succession through the full length of the probe. Earlier work^{46,47} had shown that at the light titration end point all the NO added is decomposed to $N + O$. It seems allowable therefore to include the results of the titration experiments in the NO destruction plot, as corresponding to 100 percent destruction. These points therefore are included in Fig. 7, where they fall on a straight line with the other NO destruction values below the destruction plateau, which also indicates complete NO destruction at this point.

Fig. 7 shows that under the conditions of our experiments the limiting amount of NO destruction does not coincide with the NO light titration results. A similar observation was made by Wright et.al.²² in a conventional condensed discharge flow system at high atom concentrations, but the destruction plateaus under those circumstances were larger than the titration values by a factor of at most 1.25, as compared to a factor of 2.1 observed under the present circumstances. As discussed in Section II-5, the NO destruction beyond the NO light titration end point may be attributed to N_2^* molecules.

By equating the light titration end point NO flow (3.07×10^{-6} mole sec^{-1}) to the N-atom flow, it was calculated that the stream sampled (N_2 flow through probe = 2.63×10^{-4} mole sec^{-1}) contained 1.15 mole percent atoms. For every NO molecule destroyed by



a second NO molecule would be destroyed by the N formed in (14c) through



If all or part of the NO destruction by excited molecules occurred through the intermediate formation of $NO(^4\pi)$ followed by (19)[†] or (20) and (21), then also

[†] Formation of NO_2 from NO by reaction (19) would not have been measured as NO decomposition, since the amount of undecomposed NO was determined as $NO + NO_2$ (Section IV-6).

two NO molecules were destroyed for each $\text{NO}(^4\pi)$ molecule formed (Section V-7). The difference between the NO destruction plateau and NO light titration results is 3.5×10^{-6} mole sec^{-1} . We may therefore take this difference as corresponding to a flow of N_2^* of 1.75×10^{-6} mole sec^{-1} or 0.66 mole percent of the sampled stream. However, if a second N_2^* would be needed to dissociate $\text{NO}(^4\pi)$ this above argument would not apply and the N_2^* flow could then be twice as high. Also, as discussed in Section II-5, the NO light titration value for the atom concentration may be too high and the mole fraction of atoms calculated in this section should be considered an upper bound. This implies then that N_2^{**} molecules were present. The total mole fraction of excited molecules, capable of decomposing NO, would then be higher than found above by considering only N_2^* . It should further be remarked that the mole fraction of atoms is at least two orders of magnitude larger than the ion mole fraction as measured by Langmuir probes in the free stream jet under similar circumstances.^{87,88}

The state or states of nitrogen capable of decomposing NO have already been discussed in Section V-7. Since 4.88 ev, i.e., one half the dissociation energy of N_2 , is the potential energy of recombination of N-atoms and at least the energy of $\text{A } ^3\Sigma$ ($v = 0$), 6.17 ev, is required to indirectly decompose NO, the amount of energy carried by the stream in the form of excited species capable of NO destruction is at least $(6.17/4.88) \times (0.66/1.15)$ or 0.73 times the amount of energy carried as N-atoms.

2. The Reaction with NH_3

The reaction with NH_3 did not extinguish the afterglow in the probe but somewhat diminished its intensity. The amount of NH_3 destruction was much higher than that of any of the other reactants investigated and no destruction plateau could be observed (Fig. 8). The reaction path has recently been discussed³⁶ and can probably be represented by



followed by the same process as observed photochemically^{89,90}



However, the following argument makes it likely that (23) and (24) do not represent the only NH_3 destruction path in the present system.

The energy that has to be transferred by (23) is at least 4.4 ev, the dissociation energy of the $\text{NH}_2 - \text{H}$ bond.⁹¹ Since it is likely that the N_2^1 in reaction (23) is actually $\text{A } ^3\Sigma(v \geq 0)$ (cf. Section V-6) each dissociated NH_3 molecule could be assumed to actually represent at least 6.17 ev of excitation energy, i.e., the energy of $\text{A } ^3\Sigma(v = 0)$. Assuming for the moment that the net energy[†] imparted to the stream by the discharge was equally distributed over the jet then, if formation of NH_3^* by (23) is the only path for NH_3 decomposition, at the highest NH_3 flow rate used at least 99 percent of this energy would have had to be used for the production of $\text{A } ^3\Sigma$ state molecules. It was also calculated that for the N-atom production as measured by the NO light titration (see above) 13 percent of the net discharge energy was needed; part of this energy may have been counted already since $\text{A } ^3\Sigma$ molecules were presumably also formed inside the probe by atom recombination, either directly or by way of the higher excited states. The maximum NH_3 destruction, due to atom recombination inside the probe, was 1.53×10^{-6} mole sec^{-1} , i.e., one half the light titration end point NO probe flow. Although the jet composition probably varied somewhat with the distance from the center of the jet (compare Appendix C), and for this reason the calculated energy efficiency figures may be too high by as much as a factor of two, nevertheless, an energy efficiency of at least 50 percent for the production of the $\text{A } ^3\Sigma$ state molecules inside the discharge seems unreasonably high. It therefore appears more likely that the experiments were done under conditions where secondary hydrogen atom attack on NH_3 occurred,³¹ cf. Section II-3, and consequently less energy of the active nitrogen was needed to achieve the same amount of NH_3 destruction. If this is the case, the minimum mole fraction of $\text{A } ^3\Sigma$ molecules cannot be calculated from the present NH_3 destruction data alone, since the maximum number of ammonia molecules destroyed by the secondary attack mechanism per ammonia molecule destroyed by (23) and (24) is not known. It is interesting that secondary hydrogen attack might thus occur at a reaction temperature such that the same process was not observed in a conventional flow system at lower pressures.³¹ Unless this is solely attributable to the fact that the temperature level in the present work was an average (between 900°K and 300°K), this suggests that the rate of the reaction between H-atoms and NH_3 may be critically dependent on pressure and flow conditions.

[†]i.e., the total energy minus the energy absorbed by the electrode coolant water. By measuring the flow of coolant water and the temperature of the coolant water before and after the electrodes, it was found that 46 (± 4) percent of the energy consumed by the discharge was absorbed as heat by the electrode coolant water.

3. Ratio of Excited Molecule Concentration to Atom Concentration in the Present System as Compared to Conventional Discharge Flow Systems

The observed reactivity of excited nitrogen molecules toward NO and NH₃ thus has a greater similarity with the results obtained in conventional flow systems, at high atom concentrations, than at low atom concentrations. With a condensed discharge, at high atom concentrations, a difference between the NO destruction and NO light titration was observed which was absent at the low atom concentrations obtainable with a microwave discharge.²² Similarly, in using a condensed discharge at high atom concentrations, NH₃ destruction was observed which did not occur to a measurable extent when a microwave discharge was used (compare Section II-3). Yet the relatively large excited species reactivity was observed in the present work under circumstances where the mole fraction of atoms was of the same order of magnitude as that obtainable with microwave discharges, however at pressures nearly an order of magnitude higher than used in the discussed conventional flow system studies.

As discussed in Section V-7, most of the observed excited molecules responsible for the NO reaction beyond the light titration end point probably were formed inside the discharge. Part of this excited molecule formation may have been due to atom recombination inside the discharge. Reasonable values^{11,34,92,93,94,95} for the room temperature rate constant in the expression, $-d(N)/dt = k(N)^2(N_2)$ are in the region 3×10^{-33} to 3×10^{-32} cc² mole⁻² sec⁻¹. There is some indication that the nitrogen atom recombination rate constant may have a positive temperature coefficient.⁹⁵ If we take k at 900°K (the approximate discharge temperature) as 3×10^{-31} cc² mole⁻² sec⁻¹, then about half the atoms could have undergone homogeneous recombination inside the discharge. Other mechanisms by which excited nitrogen molecules could have been formed inside the discharge are surface catalyzed recombination⁹⁶ and direct excitation.

4. The Reaction with Ethylene

The reaction with ethylene gave rise to a blue glow in the probe head and extinction of the nitrogen afterglow. The reaction therefore appeared to have gone to completion in the probe head. The results are shown in Fig. 9. The reaction led to formation of a black substance on the inner walls of the probe head. This substance was presumably a cyanogen polymer. It may be seen from Fig. 9 that the observed rate of HCN production was independent of the ethylene probe inlet flow rate over the range covered. Similar plateaus were obtained in a number of preliminary experiments under slightly different conditions.

The observed flow rate ratio (NO light titration)/(HCN production plateau) was thus 3.2. This ratio was somewhat higher than those observed in a conventional flow system in the 1 to 16 mm Hg pressure range. These latter results showed an increase in this ratio with pressure.^{18,22} Although this work seems to confirm the conventional flow system observation of a large discrepancy between both methods for measuring N-atom concentrations, this conclusion has to be considered as preliminary for the following reasons. The results of the present work were all obtained at one (average) reaction temperature. As discussed in Section II-2, the value of the HCN plateau can under certain flow conditions increase with temperature and only the temperature independent plateau achieved at higher reaction temperature can be considered to be a measure for the N-atom flow. Although the present experiments were made at an average temperature corresponding to a temperature for which the temperature independent plateau was approximately achieved in conventional flow systems, even in spherical reaction vessels,¹⁸ this was not necessarily the case for the present flow conditions. To establish whether the results of Fig. 9 represent a temperature independent plateau, obviously the temperature would have to be varied. This could probably best be done by preheating the helium-titrant gas mixture. Time limitations prevented such experiments from being made.[†]

Although in conventional flow system work^{20,21,22} at the HCN plateau, at least 95 percent of the N-containing reaction products of the active nitrogen-ethylene reaction were found to be in the form of HCN; this percentage could, a priori, be smaller at the higher pressure and different flow conditions of the present experiments. In fact, preliminary experiments indicated that a basic substance, presumably NH_3 , was trapped with the HCN. By dissolving the reaction products in H_2SO_4 and back titration with KOH (the same method as used in the NH_3 destruction experiments), this substance was found to be present in about 15 mole percent of the HCN formed. A complete analysis of the reaction products therefore seems necessary for future scavenger probe experiments using the reaction between active nitrogen and ethylene. It should be added that the formation of the cyanogen polymer, although not occurring in the same reaction in conventional discharge work at lower pressures, remains a disconcerting aspect of the ethylene reaction in the present system. Thus, although

[†] Heating the reaction zone by cutting off the helium flow would not be a satisfactory method since the fraction of the total nitrogen stream sampled would also increase (compare Section III). Since the jet composition is not uniform (compare Appendix C), the results obtained at the two temperatures would no longer be strictly comparable.

we can obtain from the experimental HCN plateau a lower bound to the nitrogen atom concentration of 0.36 mole percent, this fraction is almost certainly too low.

5. Influence of Secondary Gas Spillage on the Observed Reaction Yields

As was previously discussed, the larger portion of the secondary gas spilled out of the probe head into the external gas stream, very probably escaping around the periphery of the scavenger probe inlet orifice and shielding the external surfaces of the probe. It has been implicitly assumed that this process did not, through diffusional separation, influence the inferred NO and NH₃ destruction rates; i.e., it was assumed that the composition of the secondary gas successfully reaching the probe head reaction zone was identical to that streaming into the probe head. However, it was possible that a non-negligible portion of the scavenger gas entered the sampled gas stream by diffusion on a molecular level, in which case the helium and scavenger gas would have entered the sampled gas at different rates, probably causing the experimental results to indicate too large a scavenger gas destruction.[†] This possibility is ruled out in Appendix D on the basis of the observed NO destruction rates (Table I and Fig. 7). It has likewise been assumed that the N/N₂ and N₂^{*}/N₂ ratios were those present in the free jet and that no HCN/N₂ diffusional separation occurred subsequent to the reaction between ethylene and active nitrogen. These separation phenomena are also considered in Appendix D where it is concluded that such effects were negligible under the present set of conditions.

[†]The same arguments apply to He + C₂H₄ diffusional separation. This problem is, however, immaterial to the present discussion since it was not the C₂H₄ destruction but the formation that was measured.

APPENDIX A - ANALYSIS OF NO - NO₂ MIXTURES
DERIVATION OF FORMULAE (A) - (D) OF SECTION IV-6

In volume V₁ there were

$$\begin{array}{ll} a & \text{moles of NO} \\ a - 2a_1 - \frac{1}{2}b & \text{moles of NO}_2 \\ \frac{a(1 - a_1) - \frac{1}{2}b}{2} & \text{moles of N}_2\text{O}_4 + \\ a[1 + \frac{1}{2}b(1 + a_1)] & = X \text{ moles} \end{array} \quad (I)$$

Also

$$a[1 + \frac{1}{2}b(1 + a_2)] = Y \text{ moles} \quad (II)$$

$$K_p = \frac{(P_{\text{NO}})^2}{P_{\text{N}_2\text{O}_4}} = \left[\frac{a a_1 b P_1}{X} \right]^2 \left[\frac{X}{a(\frac{1}{2}b - \frac{1}{2}a_1 b) P_1} \right]$$

$$K_p = \frac{2a a_1^2 b P_1}{X(1 - a_1)} = \frac{2a a_2^2 b P_2}{Y(1 - a_2)} \quad (III)$$

From which

$$\frac{a_1^2}{1 - a_1} \cdot \frac{1 - a_2}{a_2^2} = \frac{V_1}{V_2} \quad (IV)$$

$$Y - X = \frac{1}{2}ab(a_2 - a_1) \quad (V)$$

From (III)

$$\frac{a_1^2}{1 - a_1} = \frac{K_p X}{2abP_1}$$

Substituting this in (IV) yields

$$\frac{a_2^2}{1 - a_2} = \frac{V_2}{V_1} \cdot \frac{K_p X}{2abP_1}$$

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which combined with (V) gives

$$\frac{a_2^2}{1 - a_2} = \frac{V_2}{V_1} \cdot \frac{K_p}{4P_1} \frac{(a_2 - a_1)X}{(Y - X)}$$

or

$$\frac{a_2^2}{1 - a_2} = \frac{V_2}{V_1} \cdot \frac{(a_2 - a_1)}{Q} \quad (\text{VI})$$

which combined with (IV) gives

$$\frac{a_1^2}{1 - a_1} = \frac{a_2 - a_1}{Q} \quad (\text{VII})$$

which may be rewritten as

$$a_2 = a_1 \{ 1 + [a_1 / (1 - a_1)] Q \} \quad (\text{B})$$

From (II)

$$a = \frac{Y}{1 + \frac{1}{2}b(1 + a_2)} \quad (\text{VIII})$$

Substituting in (V)

$$Y - X = \frac{(a_2 - a_1)bY}{2 + b(1 + a_2)} \quad (\text{IX})$$

Solving for b gives

$$b = \frac{2(Y - X)}{X(1 + a_2) - Y(1 + a_1)} \quad (\text{X})$$

which when combined with (VIII) yields

$$a = \frac{(1 + a_2)X - (1 + a_1)Y}{a_2 - a_1} \quad (\text{D})$$

Combining (X) and (D) yields in turn

$$a(1+b) = \frac{(1-a_1)Y - (1-a_2)X}{a_2 - a_1} \quad (A)$$

From (IV) and (B) we obtain

$$\left(\frac{a_2}{a_1}\right)^2 = \frac{V_2}{V_1} \frac{1-a_2}{1-a_1} = \left[1 + \left(\frac{a_1}{1-a_1}\right)Q\right]^2 \quad (XI)$$

(B) may be rewritten to give

$$1 - a_2 = 1 - a_1 - [a_1^2/(1-a_1)]Q$$

or

$$\frac{1-a_2}{1-a_1} = 1 - \left(\frac{a_1}{1-a_1}\right)^2 Q \quad (XII)$$

Substituting (XII) in (XI)

$$\frac{V_2}{V_1} \left[1 - \left(\frac{a_1}{1-a_1}\right)^2 Q\right] = \left[1 + \left(\frac{a_1}{1-a_1}\right)Q\right]^2 \quad (XIII)$$

Solving (XIII) for $\frac{a_1}{1-a_1}$ yields

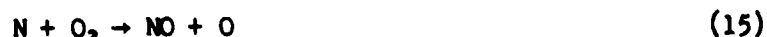
$$\frac{a_1}{1-a_1} = \frac{-1 + \{(V_2/V_1)[Q + (V_2/V_1) - 1]/Q\}^{\frac{1}{2}}}{Q + (V_2/V_1)} \quad (C)$$

A straightforward extension of the above procedures makes the derivation applicable to the case where three calibrated volumes are available; in which case, the calculations would become independent of literature (i.e., separately determined) values of K_p .

APPENDIX B - USE OF OIL PUMPED (O.P.) GRADE NITROGEN

A number of experiments were made using Airco O.P. nitrogen in order to provide some measure of comparison with some previous work^{1,2} done in this laboratory under somewhat different discharge and flow conditions and in which this grade of nitrogen was used. The experiments discussed here are not directly comparable to those of Table I, although the same discharge-flow conditions were used,[†] because they were made after a long period in which the apparatus had not been in use and during which the electrodes had become contaminated with phosphoric acid. This apparently led to a decrease in atom concentration and discharge stability and an increase in excited molecule concentration. Under these circumstances there was poor reproducibility of the measurements. The atom concentration measurements show, however, a strong difference between the two grades of nitrogen and are therefore included for the sake of completeness. The average of the results over a number of measurements are summarized in Table BI. A similar difference between the two grades of nitrogen was observed in total stream NO light titration experiments (Appendix C).

The afterglow inside the probe was already slightly blue colored, in the O.P. grade experiments, even when the secondary gas consisted only of helium. This may be attributed to O-atom formation by the reaction



followed by



Since the rate constants of (15) and of the ethylene reaction are comparable, it is possible that (15) partly suppressed the HCN formation in the O.P. grade experiments. The presence of oxygen molecules and atoms may also inhibit HCN formation.² This may explain why the NO light titration results showed less of a difference between the two grades of nitrogen than the HCN production results.

[†] For the same discharge current, voltage and nitrogen flow rate, the discharge pressure in the case of O.P. nitrogen was 2 mm Hg less than for prepurified nitrogen.

TABLE B1
INDICATED MOLE PERCENT ATOMS IN THE STREAM

<u>N₂ Grade</u>	<u>Method of Atom Determination</u>	
	<u>Limiting Yield of HCN Production</u>	<u>NO Light Titration</u>
prepurified	0.17 ± 0.01	0.85 ± 0.13
O.P.	0.096 ± 0.005	0.63 ^a

^abased on one measurement only

APPENDIX C - TOTAL STREAM COMPOSITION MEASUREMENTS
DISCHARGE ENERGY EFFICIENCY

To obtain some idea about the uniformity of the active nitrogen jet, the scavenger probe was removed and a total stream NO light titration performed for the same discharge and nitrogen flow conditions as discussed in Appendix B. Nitric oxide was introduced through a pyrex tube. The drawn out tip of this tube was centered in the jet about 10 cm downstream from the deLaval nozzle anode, which it faced. The afterglow was observed through the 45 cm long 15 cm I.D. pyrex pipe section of the test chamber which began 30 cm downstream from the nozzle exit. The titration afterglows filled the whole pyrex pipe diffusely. At test section pressures between 5.5 and 15.5 mm Hg, the titration end point was very sharp and was found to be independent of pressure.

The mole fraction of atoms in the stream, as indicated by the titration end point, was found to be 0.52 ± 0.05 percent for prepurified N_2 and 0.27 percent for O.P. N_2 , which was lower than the concentrations in the center of the jet as determined by the scavenger probe experiments discussed in Appendix B.

When the NO inlet tube was removed visual observation, at a test section pressure of 1.00 mm Hg, showed the jet to fully keep its identity without any noticeable change of jet diameter with the distance from the nozzle. For prepurified nitrogen the glow of the jet was pink, and for the O.P. grade it was orange.

Since the total N_2 flow was 7.74×10^{-3} mole sec^{-1} the total flow of N-atoms, as measured by the light titration,[†] was $0.52 \times 10^{-2} \times 7.74 \times 10^{-3} = 4.0 \times 10^{-5}$ mole sec^{-1} , and since the power dissipated in the discharge was $0.585 \text{ kw} = 0.140 \text{ Kcal sec}^{-1}$, it follows that $0.140 / (4.0 \times 10^{-5}) = 3.5 \times 10^3 \text{ Kcal}$ were used to produce one mole of N-atoms. The minimum energy needed to produce one mole of N-atoms is 112.5 Kcal, i.e., half the dissociation energy of N_2 . The energy efficiency for atom production was therefore $112.5 \times 10^2 / (3.5 \times 10^3) = 3.2$ percent. If it is assumed that the N_2^*/N ratio[‡] in the total stream is equal to that in the center portion of the stream

[†] As discussed in Sections II-5 and VI-1, the atom concentration may be lower than indicated by this technique.

[‡] Because of the contamination of the electrodes while the total stream measurements were made, this ratio had increased somewhat as compared to the experiments of Table I (compare Appendix B). The calculated energy efficiency for production of N_2^* is therefore somewhat low and correct as to order of magnitude only.

measured in the scavenger probe by the NO techniques, then it follows (compare Section VI-1) that the energy efficiency for the production of the N_2^* molecules which are capable of destroying NO was at least $3.2 \times 0.73 = 2.3$ percent.

It was found (Section VI-2) that $46(\pm 4)$ percent of the energy consumed by the discharge was absorbed as heat by the electrode coolant water. If we subtract this amount of energy from the total energy consumption than it follows that the net energy efficiency for atom production was 5.9 percent and the net energy efficiency for production of N_2^* molecules 4.3 percent.

APPENDIX B - DISCUSSION OF DIFFUSIONAL SEPARATION EFFECTS[†]

1. N/N₂ and N₂^{*}/N₂ Ratio of the Sampled Gas

Since nitrogen atoms and excited nitrogen molecules should have substantially different binary diffusion coefficients for molecular transport through N₂, it is necessary to consider the possibility that preferential diffusion to the stream tube boundary and subsequent removal by the counter flow of helium-scavenger gas mixture could have altered the ratios of N/N₂ and N₂^{*}/N₂ in the gas actually entering the reaction zone. This effect is such that the N/N₂ ratio entering the reaction zone would be somewhat smaller than that in the free stream and the N₂^{*}/N₂ ratio somewhat higher. Hence, the scavenger reaction results would tend to underestimate the N/N₂^{*} ratio actually present in the stream (i.e., overestimate the relative importance of N₂^{*}). In practice, an upper bound to this effect can be estimated by evaluating the decay of a species i, present in the entering stream tube in concentration c_i, due to diffusional transfer across a surface (of diameter d and length x) at which its concentration is maintained at a negligible level. The relevant expression for the concentration ratio c_i(x)/c_i(0) may be cast in a form analogous to that governing a first order decay process

$$\frac{c_i(x)}{c_i(0)} = \exp\left[-4 \text{Nu}_{D,ln} \cdot \left(\frac{D_{i-mix}}{\bar{u}d}\right)\left(\frac{x}{d}\right)\right]$$

where Nu_{D,ln} is the nondimensional (logarithmic mean) mass transport coefficient³⁸ and \bar{u} is the mean gas velocity in the entering stream tube. For example, the Leveque solution for laminar flow in circular conduits gives Nu_{D,ln} in the form³⁷

$$\text{Nu}_{D,ln} = 1.62 \left(\frac{\rho \bar{u} d}{\mu}\right)^{\frac{1}{3}} \left(\frac{\mu}{\rho D_{i-mix}}\right)^{\frac{1}{3}} \left(\frac{x}{d}\right)^{-\frac{1}{3}}$$

Introduction of reasonable values for the fluid dynamic and transport parameters associated with the flow in the inlet region of the probe revealed that the concentrations of either N-atoms or N₂^{*} molecules at the reaction zone could not possibly differ from their respective values in the free stream by more than a few parts per hundred due to this mechanism. While, in principle, this type of diffusional

[†]The arguments of this appendix apply equally to N₂^{*}, N₂^{**} and N₂['] molecules.

separation could be important, in practice the concentrations of atoms and excited molecules entering the reaction zone can be considered to be negligibly different from their free stream values.[†] It should also be observed that, whatever its magnitude, any diffusional separation of N_2^* and N would be essentially the same regardless of the particular scavenger gas used, since the bulk of the secondary gas flow into the probe is accounted for by the carrier gas helium (see Table I). In the present case it also follows that if separation by concentration diffusion was negligible, then separation due to pressure and thermal diffusion was likewise negligible.⁹⁸ This has been borne out by order-of-magnitude calculations using upper limits to the relevant pressure gradients, temperature gradients, and transport coefficients.

2. HCN/ N_2 Separation

Any diffusional separation of HCN/ N_2 is unlikely in view of the fact that the ethylene-active nitrogen reaction required some two to three probe diameters to go to completion. Thus, the mechanism described above, by which preferential diffusion could in principle alter the N/ N_2^* ratio reaching the reaction zone, is not available to the bulk of the product gases. Even if such a mechanism could be envisioned, a calculation similar to that carried out for the case of N/ N_2 and N_2^*/N_2 separation in the presence of scavenger gas addition would likewise reveal this effect to be negligible.

3. Errors Due to Secondary Diffusion Processes in the Absence of Scavenger Gas Addition

With regard to the theory of sampling probes in high speed streams it is conceivable that, even in the absence of scavenger gas spillage and gas phase chemical processes, pressure and temperature disturbances established by the very presence of a probe could give rise to a nontrivial distribution of atom concentration near the probe inlet due to pressure and thermal diffusion. N_2^*/N_2 separation is not expected since pressure and thermal diffusion are absent in a gas mixture whose components are of identical molecular weight.⁶⁰ A quantitative investigation of N/ N_2 separation is beyond the scope of the present report; however, the following order-of-magnitude argument suggests that this type of separation would also be negligible in the present case.

[†] considering this mechanism acting alone. The effect of chemical processes on these assumptions have already been discussed in Section V.

In the expression for the total mass flux of atoms past an arbitrary cross-section in the shock layer of thickness Δ , one can isolate terms due to a) bodily transport by convection, b) concentration diffusion, c) pressure diffusion and d) thermal diffusion. Factoring out the term due to bodily transport, the "correction" terms due to molecular transport depend upon $\Delta \text{ grad } (\ln c_1)$, $\Delta \text{ grad } (\ln p)$ and $\Delta \text{ grad } (\ln T)$, respectively. If these nondimensional gradients are themselves comparable and no larger than of order unity, then, for a weakly dissociated diatomic gas contributions (a), (b), (c) and (d) can, at most, stand in the ratio

$$1 : \frac{1}{Pe} : \frac{1}{2Pe} : \frac{\alpha_T}{Pe}$$

where the nondimensional group Pe represents a Peclet number representative of the shock layer, i.e.

$$Pe = \frac{\bar{u} \Delta}{D_{12}}$$

and α_T is the thermal diffusion factor. Current estimates⁹⁹ place the value of α_T of the order of 1.2×10^{-1} for the conditions of the present experiments. Therefore, by basing Pe on, say, half of the linear velocity immediately behind the normal shock wave, one finds the sequence $1 : 0.04 : 0.025 : 0.006$. This suggests that diffusion processes played a minor role in determining the rate of transport of atoms within the shock layer. To our knowledge this type of sampling error has not been discussed in the literature, and it would appear to represent an interesting research problem in itself.[†]

4. He/Scavenger Gas Separation in the Secondary Gas

Since helium can diffuse into active nitrogen more readily than any of the scavenger gases, S, used in this study, the question arises as to whether the helium/scavenger gas concentration ratio in the reaction zone could have been appreciably different from that in the secondary gas supply system. We will show that this was not the case, although at first sight this question seems to have to be answered in the affirmative, since in the event that molecular diffusion were the sole mechanism by which helium and scavenger gas entered the sampled gas stream the $[S]/[He]$

[†]This phenomenon could, in principle, also affect the accuracy of catalytic probes.

ratio could be altered by as much as the factor $(D_{S-N_2}/D_{He-N_2})^{2/3}$, i.e.

$$\frac{[S]_{\text{react}}}{[He]_{\text{react}}} \approx \left(\frac{D_{S-N_2}}{D_{He-N_2}} \right)^{2/3} \frac{[S]_{\text{supply}}}{[He]_{\text{supply}}}$$

which will be written

$$r' = \left(\frac{D_{S-N_2}}{D_{He-N_2}} \right)^{2/3} \cdot r$$

This relation is readily derived on the basis of a model in which the only helium and scavenger gas which finds its way into the probe does so by diffusion along a finite peripheral length of the entering stream tube of sampled gas.[†] The resulting diffusional separation ratio r/r' is probably about 2.2 for $S = NH_3$ or NO . This being the case, chemical estimates of the atom or excited molecule concentrations in the stream would be correspondingly high.[‡]

However, the nitric oxide data reveal that a negligible amount of diffusional separation took place. In Fig. 10, we have plotted^{††} the actual (chemical) rate of nitric oxide destruction, i.e., $r'\dot{n}_{He,probe} - \dot{n}_{NO,exit}$ versus actual nitric oxide flow $r'\dot{n}_{He,probe}$ entering the reaction zone, assuming several (constant) values of r/r' (0.8^{‡†}

[†] In practice, the exponent would be between 1/2 and 2/3 depending upon the velocity profile in the mixing zone.³⁸ The case 2/3 was chosen since it represents an upper limit to the magnitude of the effect.

[‡] Order of magnitude calculations showed that secondary diffusion processes (thermal and pressure diffusion) could cause only negligible changes in the helium/scavenger gas ratio entering the reaction zone. Moreover, these changes should tend to annul those produced by concentration diffusion.

^{††} To simplify the graphical representation, a smooth curve has been drawn through the origin and the NO destruction points alone, discounting the NO light titration data points. This accounts for the slight difference in initial behavior between the curve marked $r/r' = 1$ and the destruction curve given in Fig. 7. However, this difference does not alter the following argument in any way.

^{‡†} In view of the large difference between D_{He-N_2} and D_{S-N_2} (i.e., a factor of about 3.2) and the relative unimportance of secondary diffusional processes, values of r/r' less than unity are extremely unlikely. However, the value $r/r' = 0.8$ is included in Fig. 10 to display the parametric dependence of the curves for r/r' passing through unity.

through 2.2 in increments of 0.2). It is seen that for all values of $r/r' > 1$ the actual NO destruction rate passes through a maximum and becomes negative at sufficiently large values of $r'\dot{n}_{\text{He,probe}}$, which is absurd since it implies nitric oxide production at large flow rates. However, to within experimental error, the choice $r = r'$ (no diffusional separation) is the only one which yields a horizontal NO destruction plateau,[†] i.e., the only case corresponding to possible chemical behavior.

This method of data presentation indeed would allow the best value of r/r' to be determined in the presence of simultaneous chemical reaction and diffusional separation, since the apparent rate of destruction would then not plateau but continue to increase linearly ("ramp"). If this were the case, a value of $r/r' > 1$ would be required to recover the true horizontal plateau of NO destruction. In the present case, the fact that the choice $r = r'$ leads to the horizontal plateau constitutes very strong experimental evidence that in fact no appreciable diffusional separation took place in the nitric oxide destruction experiments. Moreover, in view of the closeness of the relevant binary diffusion coefficients, it immediately follows that no appreciable diffusional separation could have taken place in the ammonia destruction experiments. Thus, Fig. 8 represents a curve of actual NH_3 destruction vs NH_3 flow, and is not the result of diffusional separation alone (in the absence of chemical attack). Finally, even if r had not been equal to r' , it is clear that diffusional separation could not be the cause of apparent NO destruction beyond the NO light titration end point since the curve computed on the basis of the assumption $r/r' = 1$ (see Fig. 7) reveals that all points beyond the NO light titration end point do not lie on a straight line.[‡]

[†] The dashed lines show the locus of the individual experimental points as the ratio r/r' is continuously varied. It is observed that colinear points on any one curve are mapped to colinear points on a second curve under a change in r/r' and that the slope decreases continuously with an increase in r/r' .

[‡] Thus, in accord with the previous footnote, there is no choice of r/r' which would map all the points beyond the light titration end point to a horizontal straight line.

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TABLE I
SUMMARY OF SCAVENGER PROBE EXPERIMENTS

Experiment No.	Discharge Conditions V, mA	Scavenger Probe Conditions											
		Total H_2 Flow 10^{-3} mole sec^{-1}	Total He Flow 10^{-3} mole sec^{-1}	H_2 Flow 10^{-4} mole sec^{-1}	He Flow 10^{-4} mole sec^{-1}	H_2 Flow % of Total H_2 Flow	He Flow % of Total He Flow	He Flow (Net H_2) Flow	Probe Pressure mm Hg	Probe Temp. K	Scavenger 10^{-4} mole sec^{-1}	Scavenger Inlet Flow 10^{-4} mole sec^{-1}	Scavenger Destruction 10^{-4} mole sec^{-1}
1	930 630	7.74	2.45	2.57	4.45	3.22	18.15	0.634	18.10	498	NO	5.94	3.82
2	930 630	7.74	2.45	2.57	4.45	3.22	18.15	0.634	18.10	498	NO	3.07	3.07 ^b
3	930 625	7.74	2.45	2.57	4.56	3.32	18.63	0.640	18.10	513	NO	8.80	4.70
4	930 630	7.74	2.45	2.60	4.63	3.36	18.88	0.641	18.25	502	NO	11.09	4.73
5	930 630	7.74	2.45	2.67	4.54	3.45	18.52	0.630	18.25	506	NO	6.92	3.62
6	930 630	7.74	2.45	2.68	4.79	3.47	19.53	0.609	18.50	499	NO	17.66	6.51
7	930 630	7.74	2.45	2.71	4.64	3.50	18.94	0.631	18.35	500	NO	11.71	5.42
8	930 630	7.74	2.45	2.74	4.67	3.54	19.07	0.631	18.40	491	NO	24.55	6.54
9	930 630	7.74	2.45	2.74	4.67	3.54	19.07	0.631	18.40	491	NO	3.01	3.01 ^b
10	930 630	7.74	2.45	2.66	4.80	3.44	19.57	0.643	18.80	528	NO	34.4	6.70
11	930 630	7.74	2.45	2.66	4.80	3.44	19.57	0.643	18.80	528	NO	3.13	3.13 ^b
12	930 630	7.74	2.45	2.74	4.47	3.54	18.26	0.620	18.28	523	NH ₃	7.50	2.70
13	930 630	7.74	2.45	2.63	4.76	3.40	19.42	0.645	18.28	534	NH ₃	11.15	3.26
14	930 630	7.74	2.45	2.55	4.56	3.30	18.60	0.641	18.07	498	NH ₃	21.09	6.17
15	930 630	7.74	2.45	2.64 ^a	4.60 ^a	3.41 ^a	18.76 ^a	0.634 ^a	18.42	497	NH ₃	57.9	18.2
16	930 630	7.74	2.45	2.63 ^a	4.57 ^a	3.40 ^a	18.65 ^a	0.634 ^a	18.45	534	NH ₃	41.5	10.6
17	930 630	7.74	2.45	2.62	4.46	3.38	18.17	0.625	18.09	509	C ₂ H ₄	3.40	0.969 ^c
18	935 625	7.74	2.45	2.51	4.48	3.24	18.26	0.641	18.05	499	C ₂ H ₄	4.95	0.947 ^c
19	935 630	7.74	2.45	2.47	4.54	3.19	18.50	0.646	17.99	478	C ₂ H ₄	8.35	0.933 ^c
Avg.	930 630	7.74	2.45	2.6	4.6	3.4	18.8	0.63	18.3	503			

a. The $He/(H_2 + He)$ ratio was not determined in these experiments. Instead, the average value over all other experiments was taken as basis for the calculation of the individual H_2 and He flows.
b. The values given are the light titration end points, not actual destruction measurements.
c. The values given pertain to HCN production, not ethylene destruction.

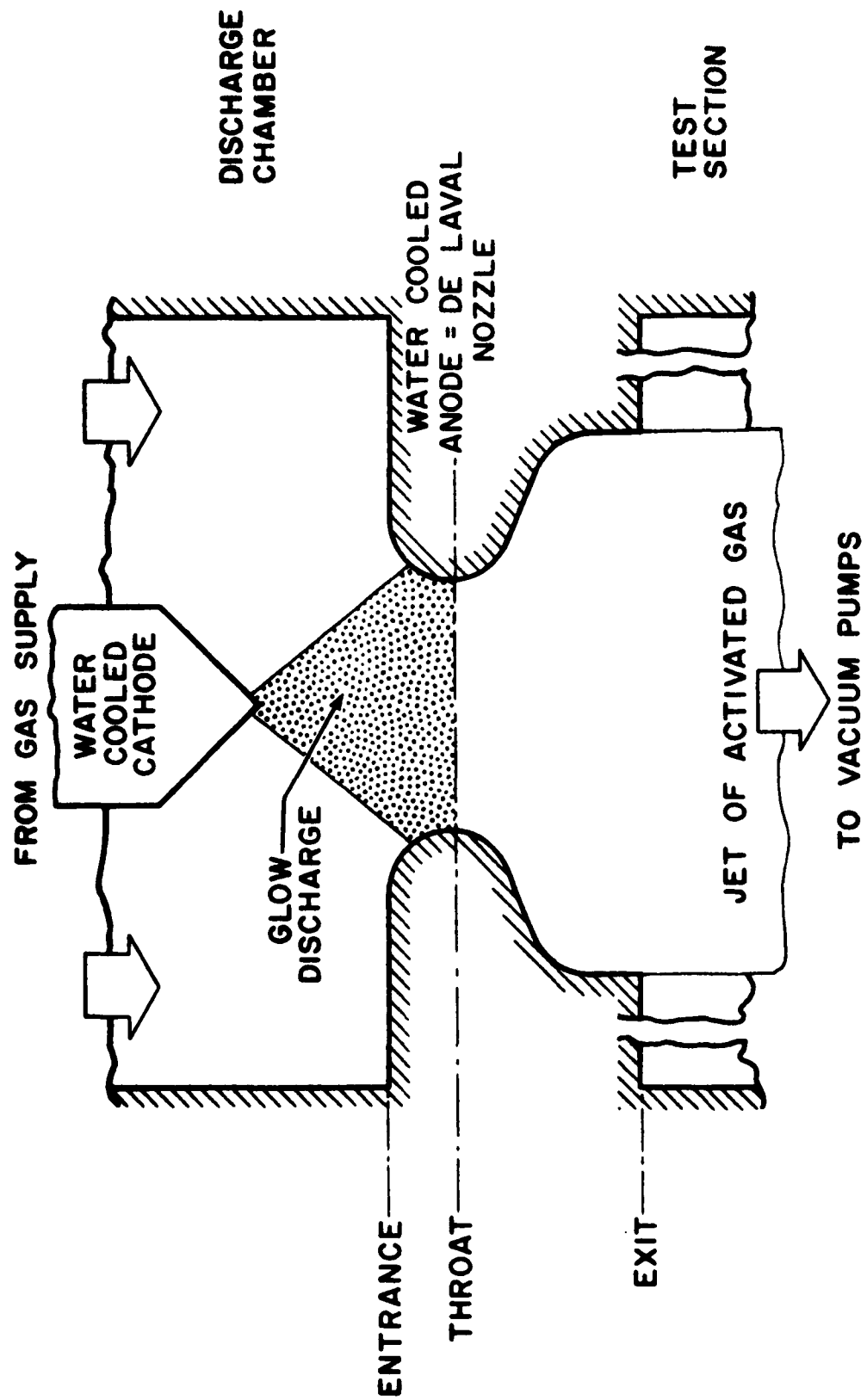


FIG. 1 SCHEMATIC OF PLASMA JET GENERATOR

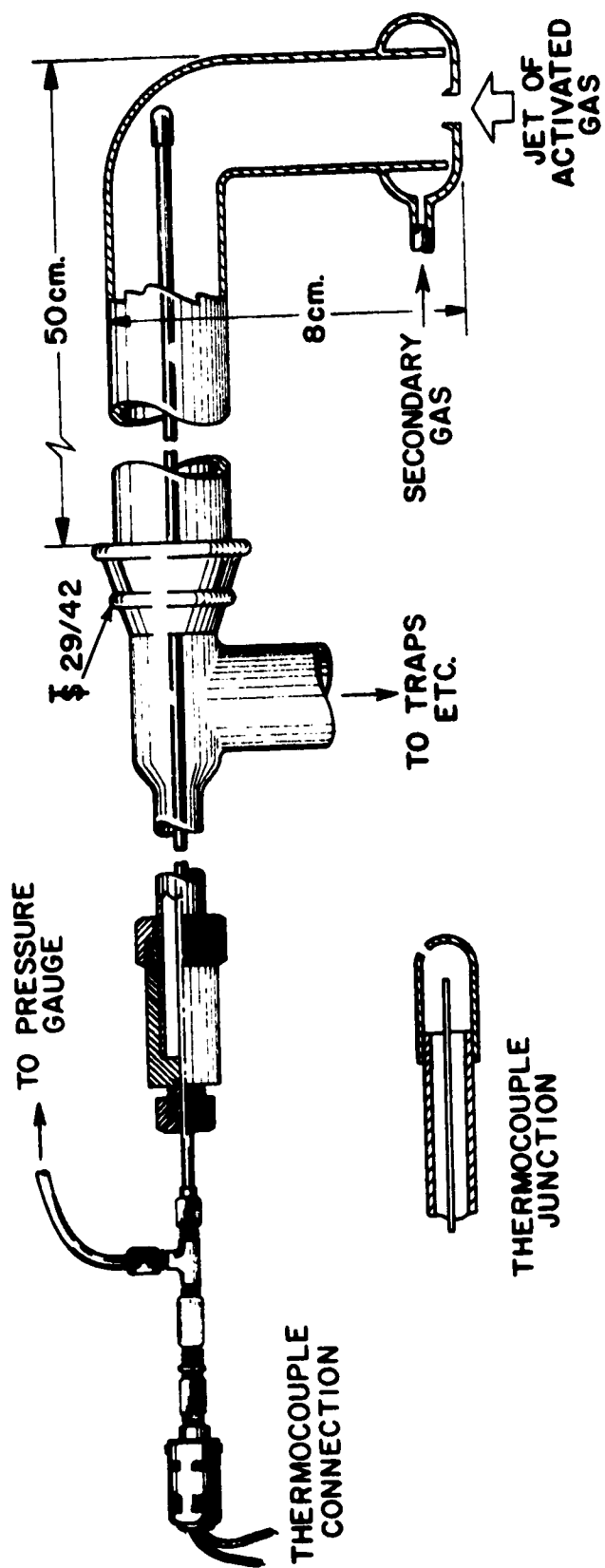


FIG. 2 CHEMICAL SCAVENGER PROBE

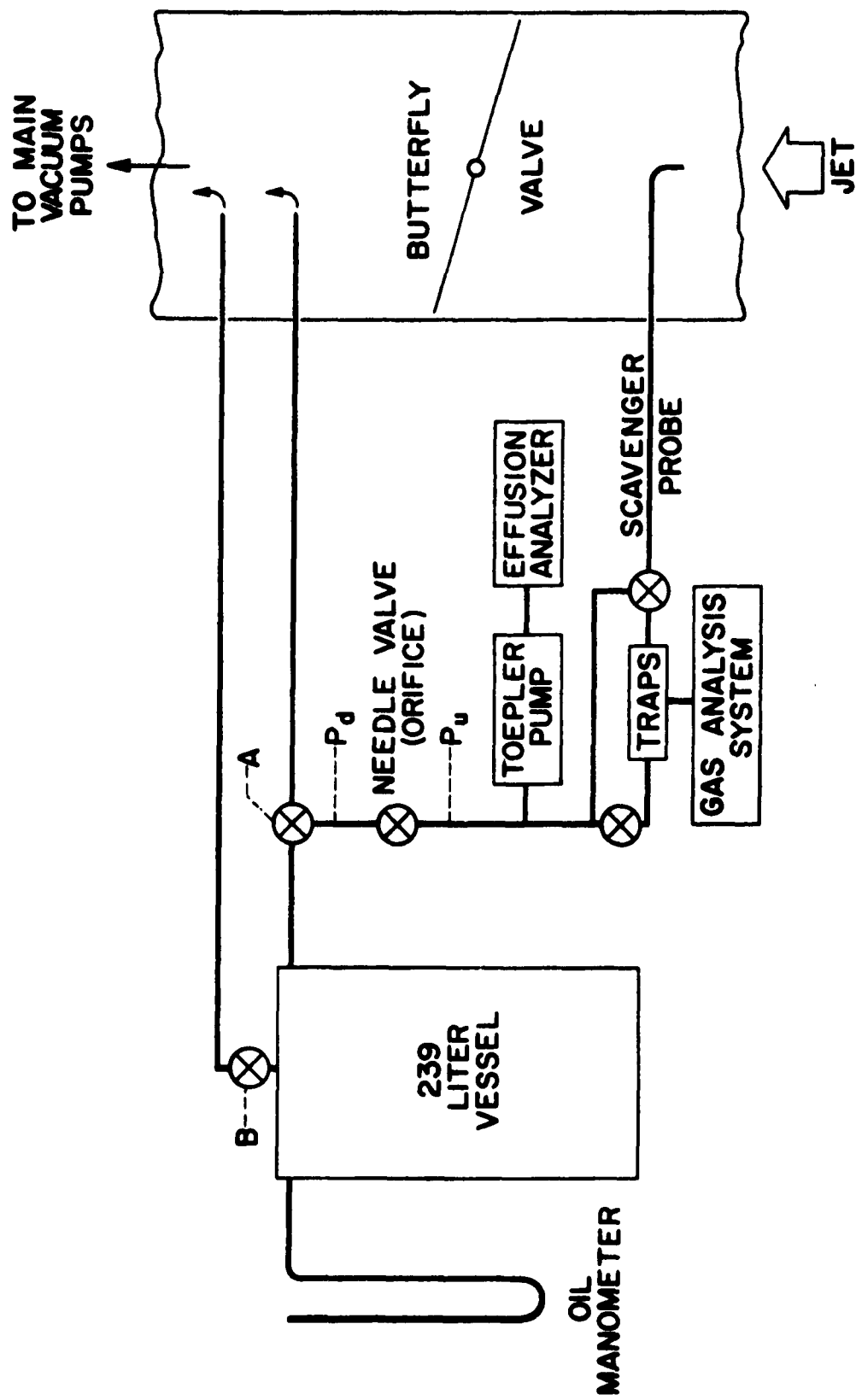


FIG. 3 CHEMICAL SCAVENGER PROBE FLOW SYSTEM

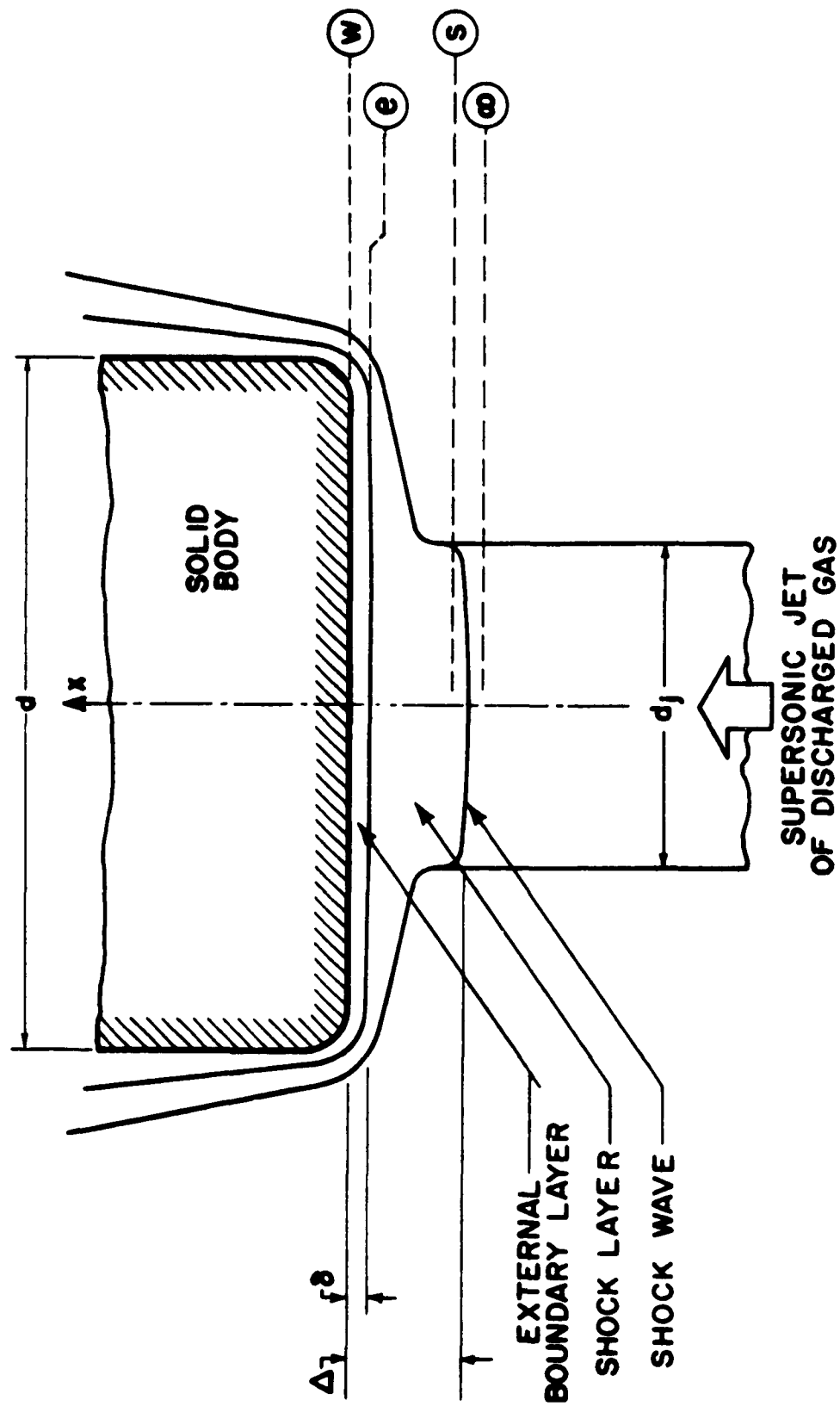
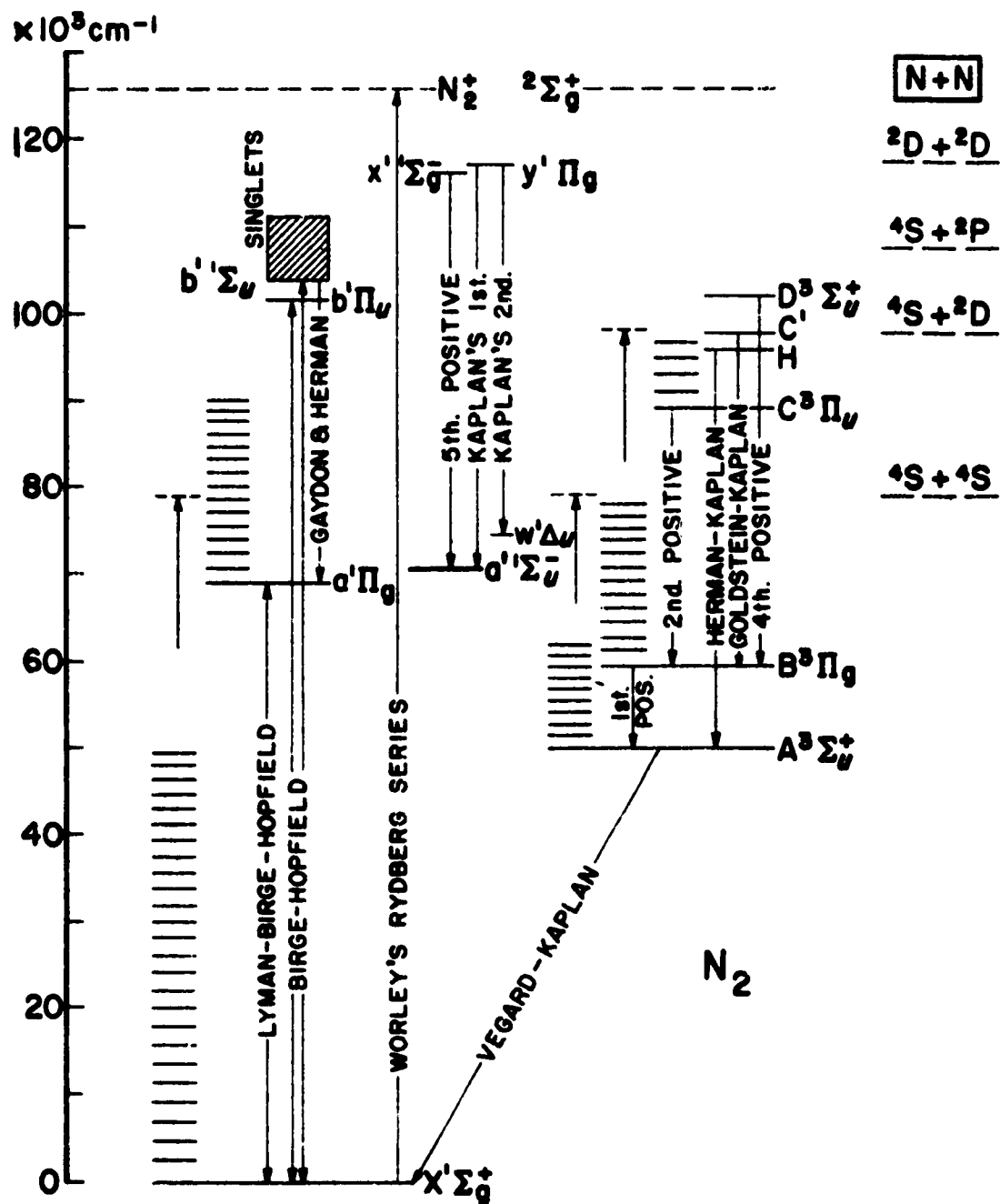


FIG. 4. FLOW FIELD IN FORWARD STAGNATION REGION OF A LARGE
FLAT-FACED SOLID BODY

FIG. 5 ENERGY LEVEL DIAGRAM OF N_2

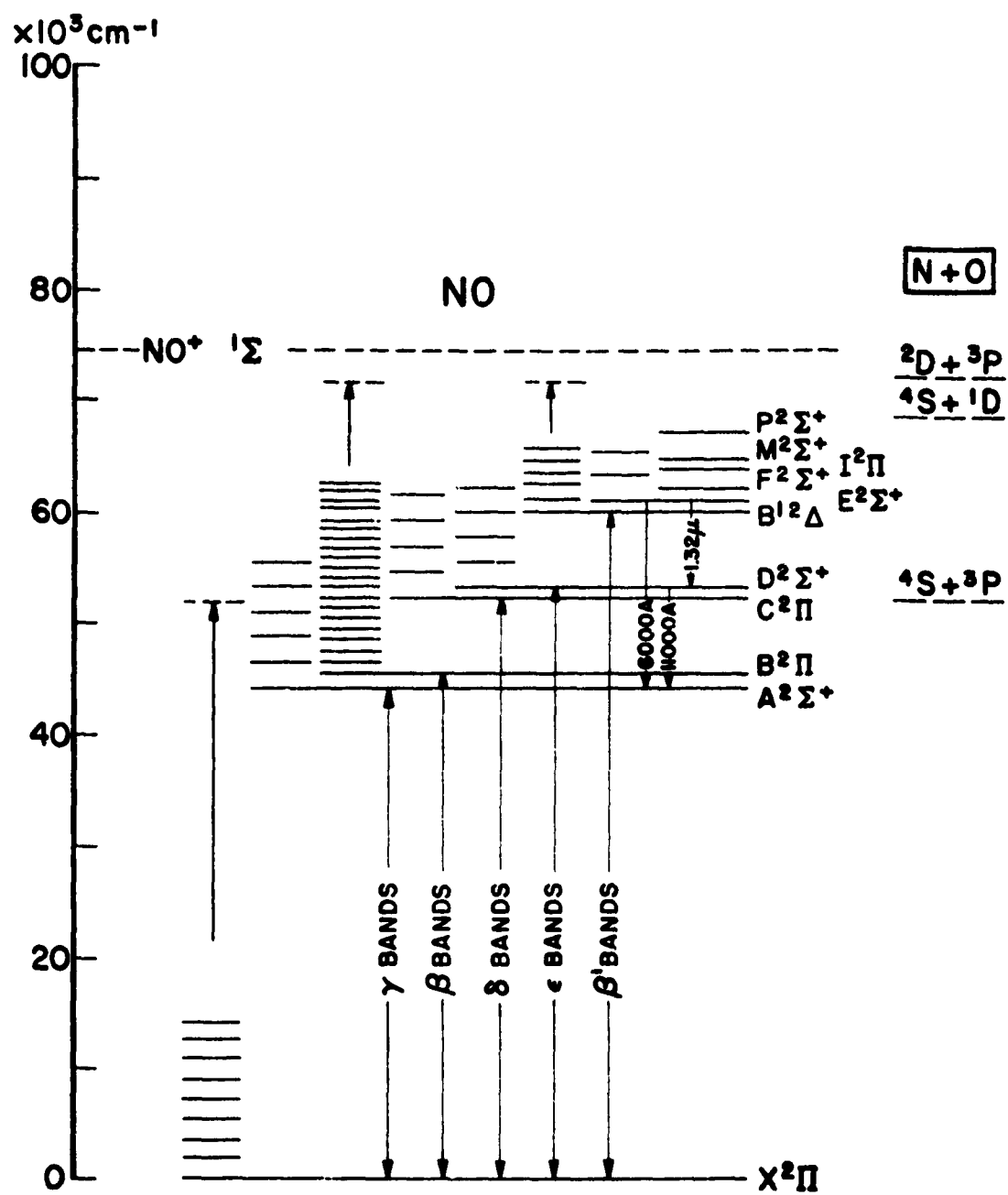


FIG. 6 ENERGY LEVEL DIAGRAM OF NO

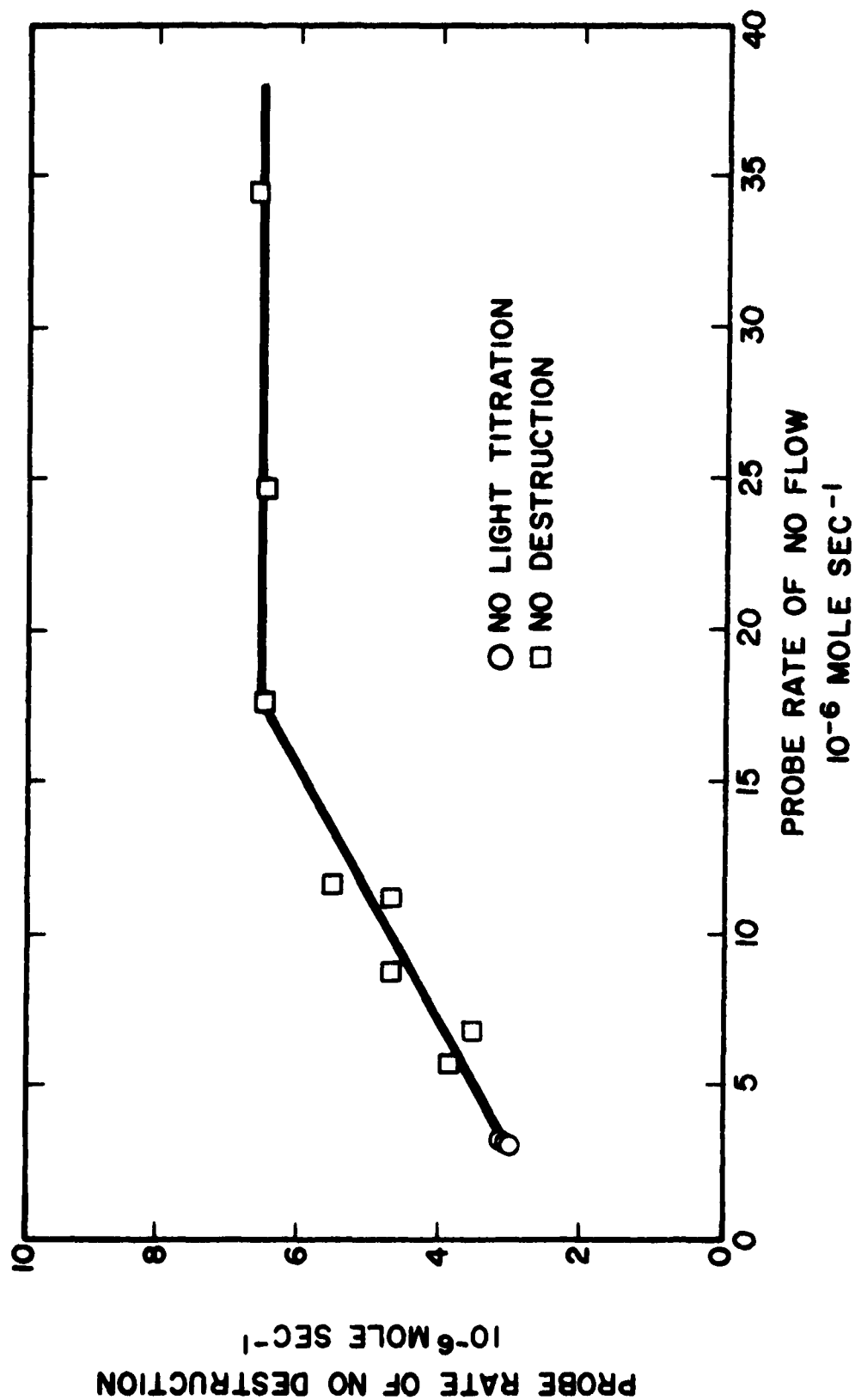


FIG. 7 NO EXPERIMENTS
Probe rate of N_2 flow: 2.6×10^{-4} mole sec $^{-1}$

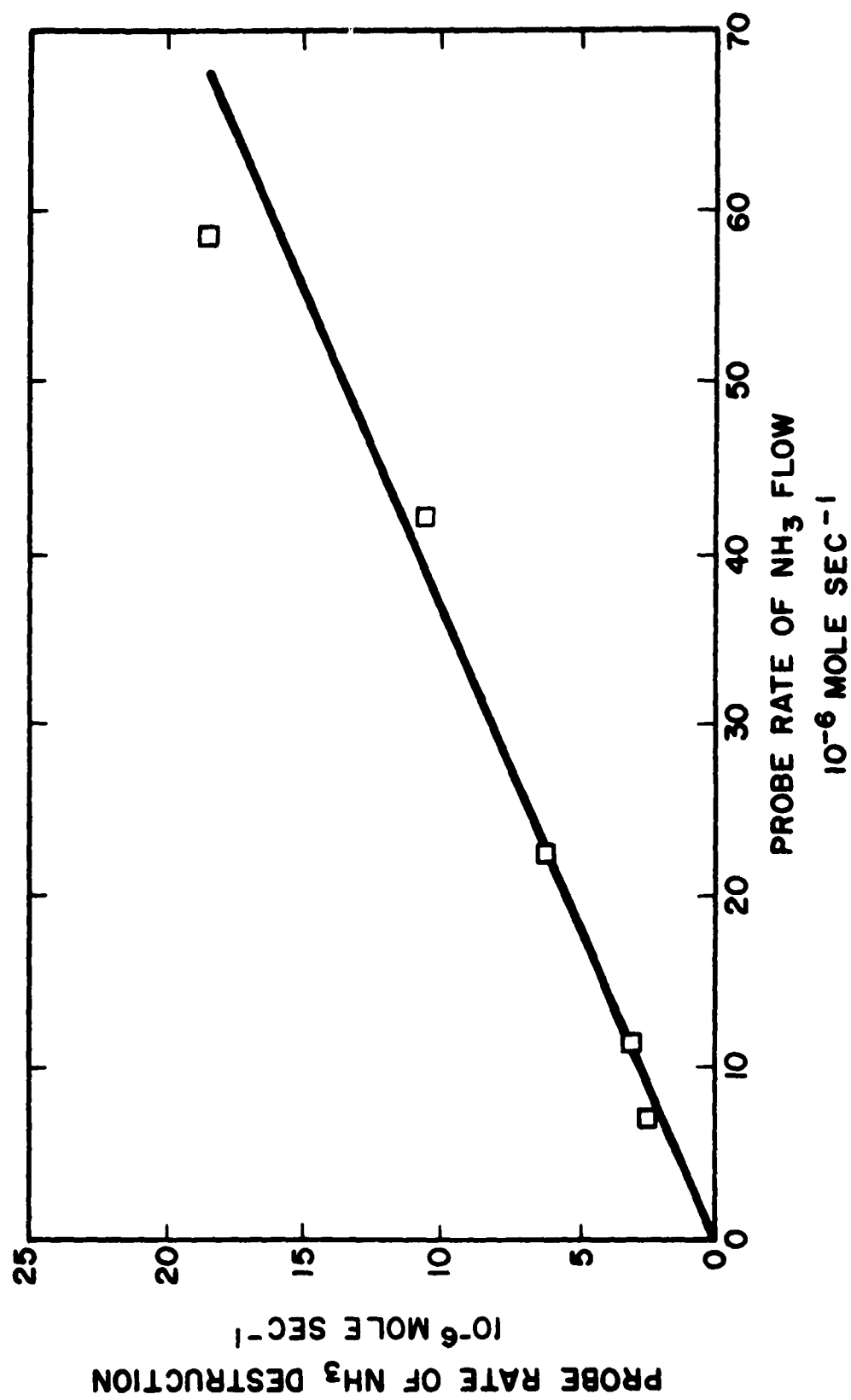


FIG. 8 NH_3 DESTRUCTION EXPERIMENTS
Probe rate of N_2 flow: $2.6 \times 10^{-4} \text{ mole sec}^{-1}$

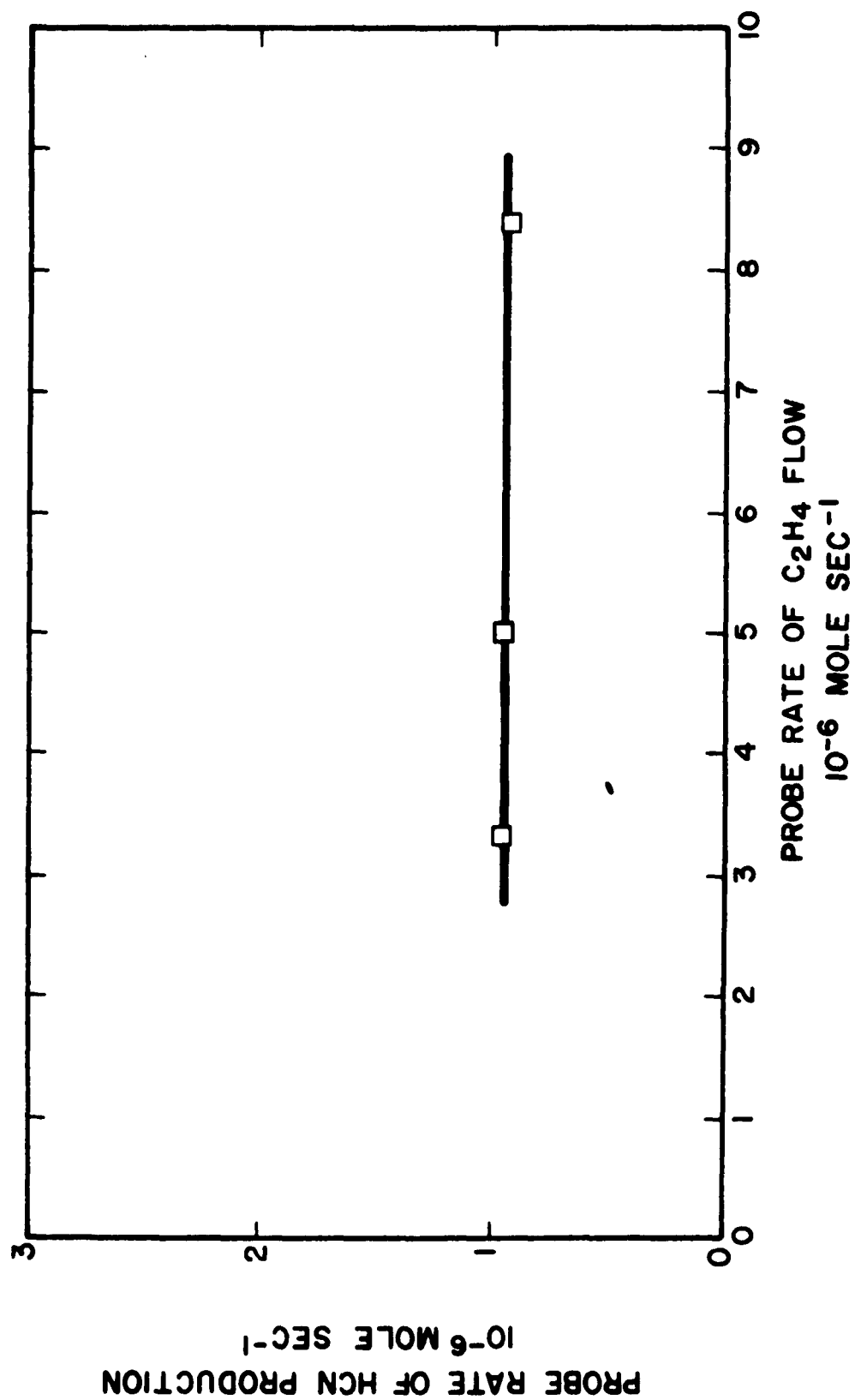


FIG. 9 HCN PRODUCTION EXPERIMENTS
Probe rate of N_2 flow: 2.6×10^{-4} mole sec^{-1}

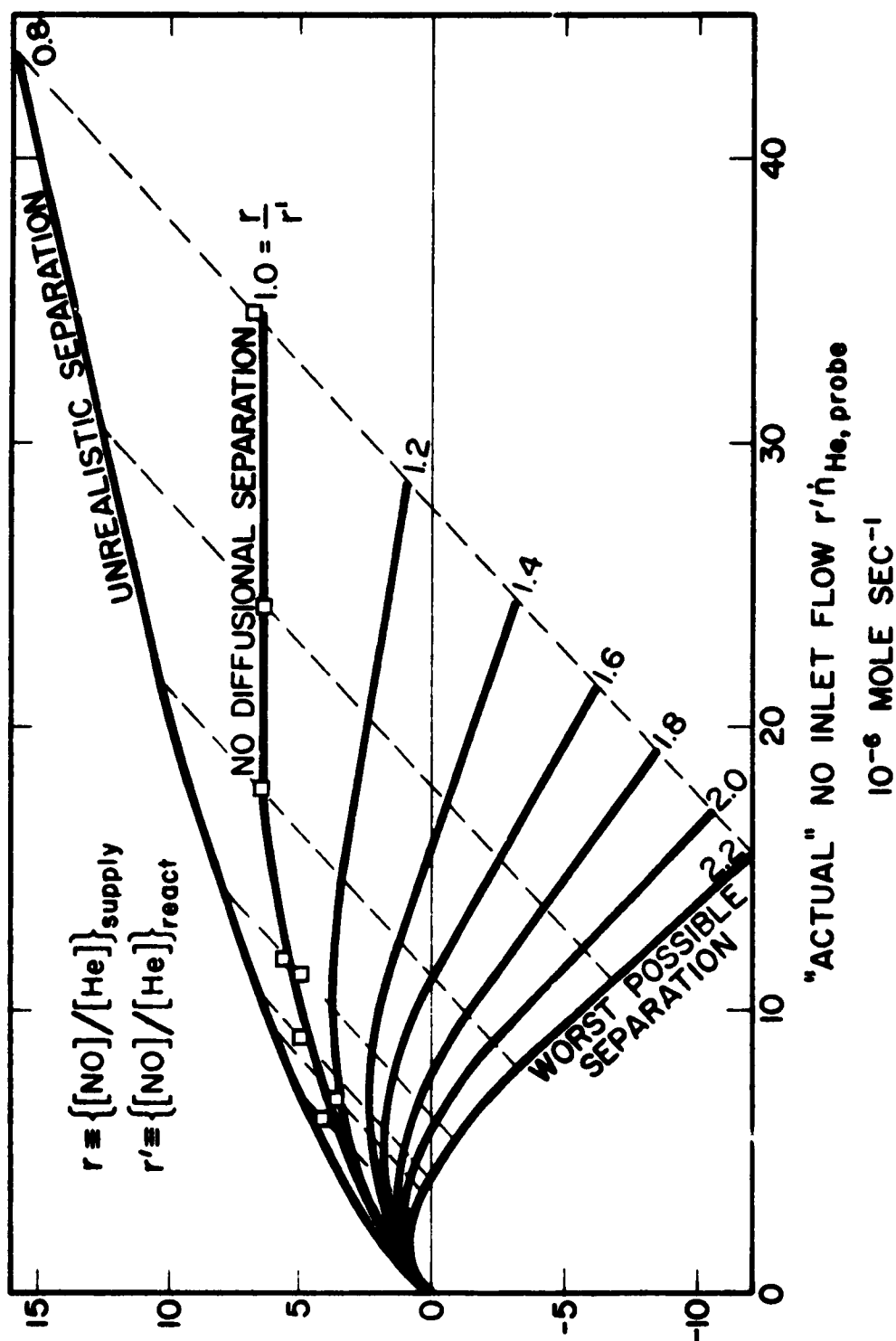


FIG. 10 HYPOTHETICAL EFFECT OF DIFFUSIONAL SEPARATION ON
NO DESTRUCTION CURVE
Probe rate of N_2 flow: 2.6×10^{-4} mole sec^{-1}